Studies of Stability constant of Synthesis of 4-((5-chloro-3-methyl-1-phenyl-Pyrazol-4-yl)methyleneamino)-2,3-dimethyl-1-phenylpyrazol-5-one with transion metal ions at 303K.

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Abstract:-

The interaction of transion metal ion with of 4-((5-chloro-3-methyl-1-phenyl-Pyrazol-4-yl)methyleneamino)-2,3-dimethyl-1-phenylpyrazol-5-one drug have been investigated by pH metric titration at 0.08 M ionic strength at room temperature in 30 % Ethanol-Water mixture. The data obtained use to estimate the values of proton-ligand stability constant (P^k) and Metal -ligand stability constant (logK). It is observed that transition metal ion form 1:1, 1: 2 complexes with all the systems.

Introduction: -

The studies of metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport f metal ion in the biological kingdom.

In the earlier papers extensive data base on metal complexes with substituted heterocyclic drugs was presented.

Narwade et.al. [1] studies the Formation and Stability constant of thorium (IV) complex with some substituted pyrazolines. Mathieu W.A. Steenland et.al.[2] studies stability constant of Cu(II) and Ni(II) complexes of trans –dioxopentaaza macrocycles in aqueous solution by different technique. Hong-Wen Gaoet.al.[3] has studied the stability constant of Cu (II) and Co (II) complexes with CNBAC in water sample spectrophotometrically. Tuba Sismanoglu [4] have studied the stability constant of binary complexes of Nicotinamide with Mn (II) by pH metrically. He also determines change in free energy, change in enthalpy and change in entropy from stability constant at different temperature. Tekade et.al. [5] have been studied complex formation of Cu (II) and Co (II) metal ion complex with substituted isoxazolines. O.Yamauchi et.al. [6] studied stability constant of metal complexes amino acids with charged side chain by pH–metrically. Hayati Sari et.al.[7] studied the stability constant of glyoxime derivative and their Nickel, Copper, Cobalt and Zinc complexes potentiometric and theoretically.

After review of literature survey the detail study of complex under identical set of experimental condition is still lacking. It was thought of interest to study the chelating properties of substituted heterocyclic drugs under suitable condition with lanthanide by pH metrically.

Experimental Details :-

The Schiff base ligands were synthesized according to literature process [10-12]. The structures were confirmed by NMR, IR and purity of these compounds was verified by TLC and melting points.

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The stock solution of Schiff base was prepared in 30 % Ethanol-Water mixture by dissolving the requisite quantity of the ligands in a minimum volume of solvent subsequently diluted to the final volume. The ligands were acidified with $HClO_4$ in a

30 % Ethanol-Water mixture and the overall ionic strength of solution was constant maintains by adding(0.1M) $NaClO_4$ The solutions were titrated with standard NaOH (0.2N) solution .
The following three solutions were titrated separately against standard NaOH
1. Free $HClO_4$ (A)
2. Free $HClO_4$ + Ligand (A+L)
3. Free $HClO_4$ + Ligand +Metal ion (A+L+M)
The pH meter reading were taken after fixed interval until stable reading was obtained and data obtained from each titration is plotted as pH Vs volume of NaOH added.

Materials and Method:-

pH measurement were carried out with equip-tronic EQ-610 pH meter (aceuracy ± 0.01 sunits) using combine glass electrode at room temperature. Metal ions solution were prepared in triply distill water and concentration estimated by standard method.[8] The solution of drug prepared in solvent .The pH metric reading in 30% ethanol – water mixture were converted to [H^+] value by applying the correction proposed by Van Uitert Haas.
The overall ionic strength of solution was constant and calculated by the equation

$$\mu = \tfrac{1}{2} C_i Z_i^2$$

The concentration of other ion in addition to Na^+ and ClO_4^- were also taken into consideration.

Result and discussion:-

Substituted heterocyclic drugs may be ionized as acid having replaceable H^+ ion from -NH group. Therefore it is represented as HL i.e.

$$HL \longrightarrow H^+ + L^-$$

The titration data used to construct the curves between volume of NaOH and P^H. They are called acid-ligand titration curves.

It is observed from titration curves for all systems ligand start deviating from the free acid curves at P^H 4.0 and deviating continuously up to P^H =11. The deviation shows that dissociation of proton in substituted drugs.

The average number of proton associated with the ligand (n_A) was determined from free acid and acid – ligand titration curves employing the equation of Irving and Rossotti [9]. The P^k values were determined from formation curves (n_A v^s P^H) by noting the P^H at which n_A =0.5. The accurate values of pk were calculated by point wise calculations which are presented in table -1. The pK values are found.

Table-1

Determination of proton- ligand stability constant (pK) at 0.08M ionic strength

System	Constant pK	
	Half integral	Point wise calculation
Ligand-2	10.82	10.50 ± 0.05

METAL -LIGAND STABILITY CONSTANT (Log k):-

Metal-ligand stability constant of transition metal ion chelate with drug were determined by employing Bjerrum calvin P^H metric titration method as adopted by Irving and Rossotti . The formation of chelate between transition metal ion with drug was indicated by the significant separation starting from pH =4.0 for transition metal ion with ligand -2.

Table-2

Determination of metal –ligand stability constant (logK) of transition metal ion with drug at 0.08M ionic strength .

System	$Logk_1$	$Logk_2$	$Logk_2 - Logk_1$	$Logk_2 / Logk_1$
Fe(II)-Ligand	4.45	6.99	2.54	1.57
Co(II)-Ligand	4.33	6.78	2.45	1.56
Ni(II)-Ligand	4.85	7.66	2.81	1.58
Cu(II)-Ligand	4.35	6.95	2.6	1.60
Zn(II)-Ligand	4.57	7.06	2.49	1.54

The result shows the ratio of $Logk_2/ Logk_1$ is positive in all cases. This implies that there is little or no steric hindrance to the addition of secondary ligand molecule .

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STUDIES OF THERMODYNAMIC STABILITY CONSTANT OF AMINO ACID WITH GD (III), YB (III) AND DY (III) COMPLEXES

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ABSTRACT
The formation of complexes has been studied by Job's method. The results obtained of stability constant were good agreement with other mathod. The metal-ligand and proton-ligand stability constant of Yb(III), Dy(III) and Gd(III) with amino acid (DL-methionine)were determined at various ionic strength by pH metric titration. $NaClO_4$ was used to maintain ionic strength of solution. The results obtained were extrapolated to the zero ionic strength using an equation with one individual parameter. The thermodynamic stability constant of the complexes were also calculated.

KEYWORD: Stability constant, ionic strength, amino acid.

INTRODUCTION
Amino acids are common components of all organisms. Protein of all species made from the amino acids. Protein plays many different biological roles in living systems. Methionine is an essential amino acid in humans. Methionine is important in angiogenesis, the growth of new blood vessels, and supplementation may benefit those suffering from Parkinson's, drug withdrawal, schizophrenia, radiation, copper poisoning, asthma, allergies, alcoholism, or depression.[1-3] Methionine is coded for by the initiation codon, meaning it indicates the start of the coding region and is the first amino acid produced in a nascent polypeptide during mRNA translation.[4] The effect of ionic strength of medium on stability constant of cu (II) complex of 2-amino-5-Chloro benzene sulphonic acid at 301K.[5] The stability constant of Co (III) with 1-Amidino-0-methylurea as primary ligand at different ionic strength.[6] The influence of ionic strength of medium on complex equilibria.[7] Association and dissociation constant of Pr (III) complexes with 3-(2-hydroxy-3-Iodo-5-methyl phenyl) 1, 5 diphenyl pyrazoline at different ionic strength.[8] Stability constant of vanadium with glycene at various ionic strength by potentiometric titration technique.[9] The stability constant of Mo (IV) with Iminodiacetic acid at different ionic strength maintain by using sodium per chlorate was investigated.[10] Effect of ionic strength and solvent effect on thermodynamic parameters.[11] They have also studied the mechanism of protonation and complex formation of binary complexes of La (III), Ce (III), Pr (III) and Nd(III) with aminopyridines. The apparent metal-ligand stability constants and confirmation of complexes studied.[13] The composition of complexes were confirmed by Job's method as modified by Vasburgh and Gold.[14]

In present work, determined the pK, metal-ligand stability constant at different ionic strength. We have studied at the 20% Dioxane-water mixture. Author thought of interest to study the effect of ionic strength on thermodynamic parameters of complexes of DL-methionine with Dy(III), Gd(III) and Yb(III) metals in 20% Dioxane-water mixture by pH metrically and spectrophotometrically.

Experimental
The pH measurements were carried out with equip-tronic EQ-610 pH meter (accuracy ± 0.01 units) using combine glass electrode at 208.15 K. Pure rare earth nitrates (99.9% Pure) was used. All metal nitrates available from Sigma Aldrich Chem. Co., U.S.A. Metal nitrate was prepared in triply distilled water and concentration was estimated by standard method. The solution of drugs was prepared in 20% 1, 4 dioxane. The pH metric readings in 20% 1, 4 dioxane–water mixture were converted to [H^+] value by applying the correction proposed by Van Uitert Haas. The 1, 4 dioxane was purified by the method described by Vogel.[12] The overall ionic strength of solution was constant maintains by adding $NaClO_4$. All the solutions were titrated with standard carbonate free NaOH (0.2N) solution at different ionic strength. The titration was carried out at ionic strength by adding $NaClO_4$ (0.02 to 0.08 M).

The experimental procedure involved pH metric titrations of solutions of

1) Free $HClO_4$ (A)
2) Free $HClO_4$ + Ligand (A+L)
3) Free $HClO_4$ + Ligand +Metal ion (A+L+M)

Data obtained from each titration is plotted as pH Vs volume of NaOH added and corresponding volume at successive pH for each set is determined and calculated.

The metal-ligand stability constant of lanthanide metals complexes with DL-methionine were investigated spectrophotometrically. The absorbances measured were carried out with Shimadzu UV-1800 ENG 240V, Japan spectrophotometer. The solutions of metal nitrates were prepared in 20% dioxane–water mixture. $NaClO_4$ was used for maintaining the constant ionic strength. The different composition of metal ion ($1x10^{-4}$M) and ligand ion ($1x10^{-4}$M) were prepared in ten series. For determination of $\lambda_{max,}$ 50% metal ion solution at which maximum absorbance observed. The absorption of all composition was measured at constant wave length (λ_{max}) and at constant pH.

RESULT AND DISCUSSION

In the present investigation the determination of proton-ligand stability constant and metal-ligand stability constant on ionic strength of medium was examined by taking fix concentration of metal nitrates and ligand solution during pH metric titration. The system has been studied at 0.02, 0.04, 0.06, 0.08M ionic strength by varying the concentration of sodium per chlorate. The total ionic strength of medium is calculated by equation.

$$\mu = \Sigma\ 1/2\ X_t Z_t^2$$

C_i , Z_i are the concentration and valences of ith ion respectively.

The values of proton–ligand and metal-ligand constant of Yb(III), Dy(III) and Gd(III) complexes at different ionic strength 0.02,0.04,0.06 and 0.08M determined. These values were determined by using Irving-Rossotties method. From table-1, it was seen that the values of proton–ligand stability constant (P^K) decreases with increasing ionic strength of medium. The metal-ligand stability constant (logK) also decrease with increasing ionic strength.

For determination of stability constant at zero ionic strength the Bronsted equarion is used.

$$logK = logK^0 + A\ \Sigma\ \Delta\ Z^2\sqrt{\mu}$$
$$pK =\ pK^0 - A\ \Delta\ Z^2\ \sqrt{\mu}$$

Where K^0 is the formation constant at zero ionic strength. pK^0 is proton-ligand stability constant at zero ionic strength . 'A' is the Debye-Huckel constant. $\Delta\ Z^2$ is the difference in square of the changes of product and reactant ion. The pK^0 and $logK^0$ values were calculated by plotting the graph of pK, $logK_1$, $logK_2$ versus $\sqrt{\mu}$.

From table-2, it was seen that the good agreement among thermodynamic constant obtained from different plots. The plots pK, $logK_1$, $logK_2$ versus $\sqrt{\mu}$ gives straight line over the entire range of ionic strength for both systems. It shows that the bronsted relationship is valid for dissociation equilibrium. Stability constant of different metal complexes with substituted acetophenone oxime at 0.1, 0.05, and 0.01M ionic strength in 70% dioxane-water mixture were studied.[15]

The conditional stability constant of Silymarin–lanthanide metals complexes were determined for all systems by using equation.

K= x / (a_1-x) (b_1-x) = x / (a_2-x) (b_2-x)
K= Conditional stability constant, x = Concentration of complex, a_1 and b_1 were concentration of metal ion and ligand before dilution. The concentration of metal ion and ligand after dilution were a_2 and b_2. The values of 'x' were calculated from graph optical density V^s % composition of metal ions in solution.

From table-3, it was seen that the good agreement among thermodynamic constant obtained from pH metry and spectrophotometrically.

Table-1. Proton-ligand (pK) and metal-ligand stability constant (Log K) values for Yb(III), Dy (III) and Gd(III)with DL-methionine at various ionic strength(μ)

μ	$\sqrt{\mu}$	$\sqrt{\mu}/1+\sqrt{\mu}$	$[\sqrt{\mu}/1+\sqrt{\mu}] -0.3\sqrt{\mu}$	pK	$LogK_1$	$LogK_2$
DL-methionine + Yb(III)						
0.02	0.1414	0.1239	0.0815	7.8074	7.15	4.45
0.04	0.2000	0.1667	0.1067	7.6267	6.65	4.30
0.06	0.2450	0.1968	0.1233	6.8782	6.35	3.60
0.08	0.2828	0.2205	0.1356	5.8940	5.70	3.75
DL-methionine + Dy(III)						
0.02	0.1414	0.1239	0.0815	7.7164	6.90	4.30
0.04	0.2000	0.1667	0.1067	7.6287	6.70	3.65
0.06	0.2450	0.1968	0.1233	6.7752	6.55	3.60
0.08	0.2828	0.2205	0.1356	5.8940	5.40	3.35
DL-methionine + Gd(III)						

0.02	0.1414	0.1239	0.0815	7.6014	7.15	4.35
0.04	0.2000	0.1667	0.1067	7.5237	6.60	4.10
0.06	0.2450	0.1968	0.1233	6.8772	6.15	3.70
0.08	0.2828	0.2205	0.1356	5.6940	6.05	3.15

Table-2. Thermodynamic stability constant (pK^0 and Log K^0) values for Yb(III), Dy (III) and Gd(III) with DL-methionine

System		P^K Vs $\sqrt{\mu}$
DL-methionine + Yb(III)	PK^0	9.9423
	Log K$_1^0$	8.5829
	Log K$_2^0$	5.3306
DL-methionine + Dy(III)	PK^0	9.8166
	Log K$_1^0$	8.4297
	Log K$_2^0$	5.1004
DL-methionine + Gd(III)	PK^0	9.7318
	Log K$_1^0$	8.2512
	Log K$_2^0$	5.6287

Table-3. Metal-ligand stability constants (Log K) values obtained by pH-metry and Spectrophotometry technique (Ionic strength = 0.08m)

System	pH metry	Spectrophotometry
Yb (III)+ DL-methionine	3.75	3.8033
Dy (III)+ DL-methionine	3.35	3.4205
Gd (III)+ DL-methionine	3.15	3.2234

Fig.1 Plot of pK Vs √μ

Fig.3 Plot of logk$_2$ Vs √μ

Fig.3 Plot of logk$_1$ Vs √μ
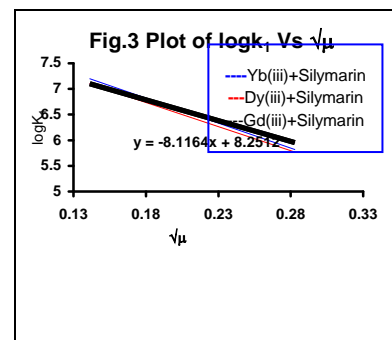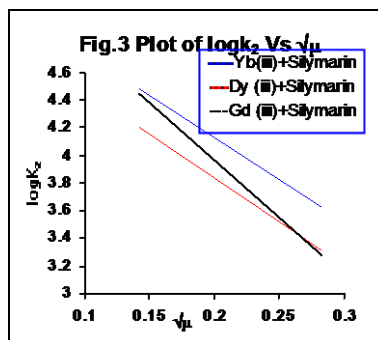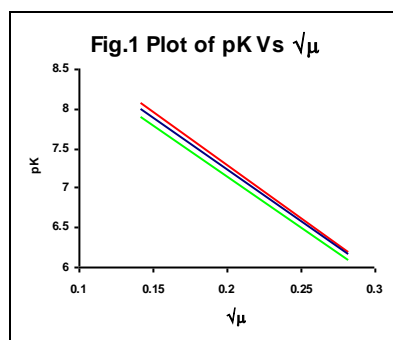
CONCLUSION
The calculated values of stability constant at various ionic strength are high. From data the conclusion is, the complexes of Silymarin with Yb (III), Dy (III), Gd (III) metal ions were quite stable at over all range of ionic strength. The values of thermodynamic parameters are nearly same from all plots was good agreement of results. The values of conditional metal-ligand stability constant shows good agreement with the values determined by pH metrically.

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ULTRASONIC VELOCITY, DENSITY MEASUREMENTS OF （E）-2- HYDROXY -3-（4 - HYDROXY -5- ISOPROPYL -2- METHYL PHENYL）DIAZENYL）NAPTHALENE 1-4-DIONE IN MIXED SOLVENT AT 303.15 K

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ABSTRACT
The acoustical properties have been investigated from the ultrasonic velocity and density measurements of azo compound in 10% DMSO at 300.15K. The measurement have been perform to evaluate acoustical parameter such as adiabatic compressibility ($\Box$s), Partial molal volume ($\Box$v), intermolecular free length (Lf), apparent molal compressibility ($\Box$k), specific acoustic impedance (Z), relative association (RA), solvation number (Sn).

KEYWORD: *Ultrasonic velocity, viscosity, adiabatic compressibility, apparent molal volume.*

INTRODUCTION
Azo compounds are a very important in the field of research. They are highly colored and have been used as dyes and pigments for a long time. In fact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts.[1, 2] In the recent years, measurements of the Ultrasonic velocity are helpful to interpreted solute-solvent, ion-solvent interaction in aqueous and non aqueous medium.[3-9] Fumio Kawaizumi[10] have been studied the acoustical properties of complex in water. Jahagirdar et. al. has studied the acoustical properties of four different drugs in methanol and he drawn conclusion from adiabatic compressibility. The four different drugs compress the solvent methanol to the same extent but it shows different solute-solvent interaction due to their different size, shape and structure.[11] Meshram et. al. studies the different acoustical properties of some substituted Pyrazolines in binary mixture acetone-water and observed variation of ultrasonic velocity with concentration.[12] Palani have investigated the measurement of ultrasonic velocity and density of amino acid in aqueous magnesium acetate at constant temperature.[13] The ion-dipole interaction mainly depends on ion size and polarity of solvent. The strength of ion-dipole attraction is directly proportional to the size of the ions, magnitude of dipole. But inversely proportional to the distance between ion and molecules. Voleisines has been studied the structural properties of solution of lanthanide salt by measuring ultrasonic velocity.[14] Syal et.al. has been studied the ultrasonic

velocity of PEG-8000, PEG- study of acoustical properties of substituted heterocyclic compounds under suitable condition.[15] Tadkalkar et.al. have studied the acoustical and thermodynamic properties of citric acid in water at different temperature.[16] Mishra et.al. have investigated ultrasonic velocity and density in non aqueous solution of metal complex and evaluate acoustic properties of metal complex.[17] M. Arvinthraj et.al. have determined the acoustic properties for the mixture of amines with amide in benzene at 303K-313K. They also determined thermodynamic parameters.[18] S.K. Thakur et.al. have studied the different acoustical parameters of binary mixture of 1-propanol and water.[19] Mirikar et.sal. studied the molecular interaction between liquids.[20]

After review of literature survey the detail study of azo cpomound under identical set of experimental condition is still lacking. It was thought of interest to study the acoustical properties of substituted heterocyclic drug under suitable condition.

Experimental
In the present study, the azo compound was used. The double distilled DMSO was used for preparation of different concentration of drug solution. The densities were determined by using specific gravity bottle by relative measurement method with accuracy $\Box$ 1x10^{-5} gm/cm^{3}. The ultrasonic velocities were measured by using ultrasonic interferometer having frequency 3MHz. The constant temperature was maintained by circulating

water through the double wall measuring cell, made up of steel.

In the present investigation, different properties such as adiabatic compressibility ($\Box$s), apparent molal volume ($\Box_v$), intermolecular free length (L_f), apparent molal compressibility ($\Box_\Box$), specific acoustic impedance (Z), relative association (R_A), solvation number(S_n).

RESULTS AND DISCUSSION
In the present investigation, different acoustical properties such as ultrasonic velocity (Us), adiabatic compressibility ($\Box$s), intermolecular free length (L_f), specific acoustic impedance (Z), are listed in table-1. Partial molal volume ($\Box_v$), apparent molal compressibility ($\Box_\Box$), relative association (R_A), solvation number (Sn) are listed in table-2. It was found that the ultrasonic velocity decreased with the increase in concentration for system (Table-1). Variation of ultrasonic velocity in solution depends upon the increase or decrease of molecular free length after mixing the component. This is based on a model for sound propagation proposed by Eyring and Kincaud[13]. Intermolecular free length increased linearly on increase in concentration of azo compound in 10% DMSO. Hence, decreased in ultrasonic velocity with increase in concentration of drug. It happened because there was significant interaction between ions and solvent molecules suggesting a structure promoting behavior of the added electrolyte. The specific acoustic impedance (Z) increased with the decrease in concentration of azo

compound in 10% DMSO. When concentration of electrolyte was increased, the thickness of oppositely charged ionic atmosphere increases due to decrease in ionic strength. This is suggested by decrease in acoustic impedance with concentration in system. It was seen that the intermolecular free length increased with the increase in concentration in system. The intermolecular free length increased due to greater force of attraction between solute and solvent by forming hydrogen bonding. The adiabatic compressibility increased with the increase in concentration of solution. It happened due to collection of solvent molecule around ions, this supporting weak ion-solvent interaction. This indicates that there is significant solute-solvent interaction.

It was observed that apparent molal volume increased with concentration in system. It indicates the existence of strong ion-solvent interaction. It was found that the value of apparent adiabatic compressibility was increased with the increase in concentration of azo compound in DMSO. It shows strong electrostatic attractive force in the vicinity of ions. From the data, we were concluded that strong molecular association was found in azo compound. The value of relative association increased with the increase in concentration in system. It has been found that there was strong interaction between solute and solvent. There were regular increases in solvation number with the increase in concentration; it indicates the solvent molecule forms strong coordination bond in primary layer. It indicates the increase in size of secondary layer of Solvation.

Table 1: Ultrasonic velocity, density, adiabatic compressibility ($\Box_S$), Specific acoustic impedance (Z) Intermolecular free length (L_f).

Concentration moles lit^{-1} (m)	Density (ds) kg m^{-3}	Ultrasonic velocity (Us) m s^{-1}	Adiabatic compressibiliy ($\Box_S$) x10^{-10} m^{2}N^{-1}	Intermolecular free length (L_f) x10^{-11} m	Specific acoustic impedance (Zx10^6) kg m^{-2} s^{-1}
1x10^{-3}	1006.11	1431.48	3.40913	3.71346	1.4402
2x10^{-3}	1012.56	1443.87	3.32212	3.66577	1.4618
3x10^{-3}	1016.86	1458.44	3.22355	3.61097	1.4823
4x10^{-3}	1021.91	1471.72	3.13707	3.56221	1.5026
5x10^{-3}	1024.41	1487.21	3.04007	3.50670	1.5229
6x10^{-3}	1028.12	1499.37	2.96676	3.46416	1.5413
7x10^{-3}	1034.26	1519.65	2.84950	3.39502	1.5718
8x10^{-3}	1039.61	1536.54	2.75947	3.34095	1.5959
9x10^{-3}	1046.29	1559.23	2.63797	3.26657	1.6310

Table 2: Concentration (m), Relative association (R_A), Apparent molal compressibility ($\Box_\Box$), Apparent molal volume ($\Box_v$), Solvation number (S_n).

Concentration(m) moles lit^{-1}	Apparent molal volume (-ϕ_v) m^{3}mole^{-1}	Apparent molar compressibility (ϕ_k)x10^{-10} m^2 N^{-1}	Relative association (R_A)	Solvation number (S_n)
1x10^{-3}	14.0338	1.1985	1.0491	0.67554
2x10^{-3}	9.3777	1.1676	1.0110	0.65811
3x10^{-3}	7.6777	1.1326	1.0095	0.63836
4x10^{-3}	6.8789	1.1018	1.0099	0.62103
5x10^{-3}	6.0094	1.0673	1.0076	0.60159
6x10^{-3}	5.5855	1.0413	1.0074	0.585910

7x10^{-3}	5.5473	0.9996	1.0065	0.56342
8x10^{-3}	5.3950	0.9676	1.0059	0.54539
9x10^{-3}	5.4760	0.9244	1.0052	0.52106

CONCLUSION

The present study shows the experimental data for ultrasonic velocity, density and viscosity at 300.15K for substituted heterocyclic azo compounds in 10% DMSO. From experimental data, the acoustical properties were calculated. The solute-solvent interaction and ion-ion / solute-solute interaction existing between compound and DMSO were also studied with the help of experimental data. Lastly it has been concluded from the experimental data, that the solute-solvent interaction in system are weak..

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Dielectric behavior of gel grown barium oxalate

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Abstract: Barium oxalate crystals have been grown by gel method using agar gel as a media of growth at ambient temperature using single diffusion technique. Best results were obtained when a gel was set by mixing a solution of different concentration and quantity of ammonium chloride as an additive. A single crystal of about 10 times larger than the crystal obtained in various other methods at the interstitial in a tube associated 8.5 mL NH_4Cl additive solution. Various polarization mechanisms such as atomic polarization of lattice, orientation polarization of dipoles and space charge polarization in the grown crystals have been understood using results of the measurements of dielectric constant (ϵ') and dielectric loss ($tan\delta$) as functions of frequency and temperature. Ion core type polarization is seen in the temperature range 150 –175°C, and above 175°C, there is interfacial polarization for relatively lower frequency range. One observes dielectric dispersion at lower frequency presumably due to domain wall relaxation.

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I.   INTRODUCTION

There has been constant urge for growing high quality and defect free large size single crystals. In recent years, crystal growth in gel medium has attracted much attention because of their simplicity [1-2] and found unique place due to its characteristics of suppression of nucleation centers [3]. Most oxalates and molybdates have wide applications in electro- and acousto-optical devices [4-6]. Oxalates have vital applications as a biosensor [7]. They used to improve the hardness of barium or strontium titanate and to achieve decreased layer thickness in multilayer ceramic capacitors [8]. They also have good ionic conductivity [9], exhibit applications as precipitation agent [10] as well as used in nano particle synthesis, in magnetic and luminescent devices [11-13]. The metal di-carboxylate like cadmium oxalate is fairly suitable as a stabilizer [14] of PVC. A study of magnetic behavior of solid gives valuable information about their use as an insulator and for various other mechanical and electrical properties. The magnetic susceptibility provides information [15, 16] on magnetic moment. Ionic crystals [17-20] have interesting features regarding indirect band-to-band transitions. Since the data on dielectric properties of barium oxalate crystal do not exist in the literature, however dielectric property of barium oxalate pallet is reported [21]. In the present work dielectric behavior of a crystal is investigated by the measurements of the dependence of dielectric constant as well as tangent loss on applied frequency and environmental temperature as external parameter.

II.   EXPERIMENTAL

Barium oxalates in the form of single crystals were prepared by employing controlled ionic diffusion through agar gel [22, 23]. In previous study, heavy nucleation was reported in agar gel method.[24, 25]. To further control nucleation and to improve size of crystal NH_4Cl was used as an additive impurity   [26, 27]. Best results were obtained when a tube is associated with 8.5 mL NH_4Cl additive solution. A large single crystal about 10 times larger than the reported at the interstitial is obtained as shown in **Figure 1**. For present study well facet, transparent crystals of size between $4 \times 2 \times 0.5$ mm^3 and $20 \times 15 \times 5$ mm^3 were used. Crystalline nature of the grown crystal was confirmed by X-ray diffraction. The crystal is found to be a monoclinic perovskite structure. The computed unit cell dimensions are

$a = 0.907$ nm, $b = 0.924$ nm, $c = 0.953$ nm
$\alpha = 90°$, $\beta = 114.8°$, $\gamma = 90°$

Their EDAX trace showed prominent barium peak, and their pycnometric density was found to be 2.680gcm. For the present study, a crystal with prominent (100) grown face was mounted between a pair of flat stainless steel electrodes. The capacitance was measured in the temperature range 30–230°C applying a constant a.c. frequency ranging 20 KHz to 1MHz using a specially constructed sample holder. It may be noted that the

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holder was not evacuated. The variation in temperature was carried out after enclosing the cell in a resistance heated muffle furnace, while the sample temperature was monitored using a chromel–alumel thermocouple (± 1°C). The temperature was increased by regulating the input power through 'AE' make 15-amp dimmerstat, the rate of heating was maintained linear (40°C/h). The capacitance measurements were made using 'Hewlett Packard' 4284A LCR meter. The schematic diagram of experimental setup is as shown in **Figure 2**.The measured values of the capacitance were converted into dielectric constant and dissipation factor by determining the area and thickness of the crystal.
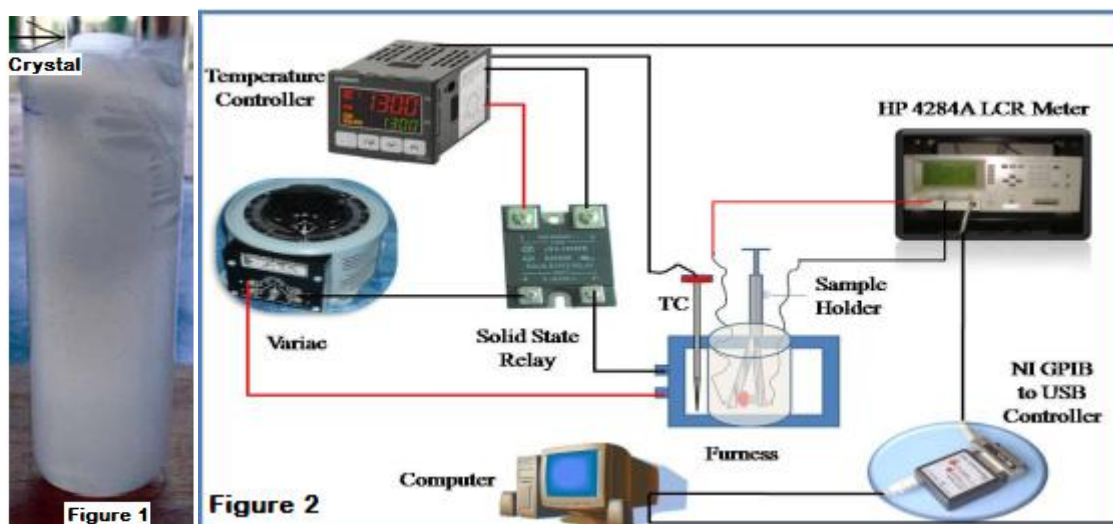
Figure 1: Barium oxalate crystal grown at the interstitial using NH_4Cl as an additive
Figure 2: Experimental setup for Dielectric measurement

III. RESULTS AND DISCUSSION

The data on measurements in respect of temperature and frequency dependence of both dielectric constant and the dissipation factor of barium oxalate single crystals have been plotted graphically in **Figures 3–10**. The temperature dependence of dielectric constant and tanδ in the present case manifests pyro electric behavior of the crystals.

I. Variation of dielectric constant with temperature at constant frequency
The observed dielectric constant versus temperature at fixed applied a.c. frequencies from 20 KHz to 1MHz were plotted and shown in four different figures from **Figure 3 to 6**. The following points are noteworthy:
(i)   The value of dielectric constant is decreasing with rising in temperature.
(ii)   Variation in maximum value of dielectric constant is observed at different constant frequencies. The maximum value of dielectric constant is observed for lower constant frequencies in the range 1040 to 840. It remains constant nearly at 840 for intermediate frequencies, while lowest nearly at 820 for higher frequencies.
(iii)   The dielectric constant in lower temperature region was found to be decreasing with increasing the constant applied a.c. frequencies.
(iv)   The minimum dielectric constant ϵ' 720 at 150⁰C are nearly same for all constant frequencies.
(v)   Above transition temperature 150⁰C, there is gradual increase in the value of dielectric constant (ϵ').

II. Variation of Dielectric loss with temperature at constant frequency:
Figure 7 shows the dependence of dielectric loss on temperature under constant applied a.c. frequencies ranging between 40 to 500 KHz and similar dielectric loss is observed in the range520 KHz to 720 KHz as in **Figure 8**. The nature of the curves show-
(i)   The dielectric loss decreases as the applied constant a.c. frequency increases at a particular temperature.
(ii)   **Figure 7** and **8** shows dielectric loss less than 0.01 nearly at 150⁰C and then gradually increases with rise in temperature for all range frequencies.

III. Variation of Dielectric constant with frequency at constant temperature:
The dependence of dielectric constant at different frequencies under constant temperature 30⁰ to 230⁰C is shown in **Figure 9.** The following points may be noteworthy:
(i)   The dielectric constant decreases as the frequency increases at all constant temperature.
(ii)   The dielectric constant is minimum almost at 300KHz then slightly increases upto 320KHz Sand decreases and then remains nearly constant at all above frequencies for constant temperatures.

IV. Variation of Dielectric loss with frequency at constant temperature

The dependence of dielectric loss at different frequency at the constant temperature 30^0 to 230^0C is revealed in a plot of dielectric loss versus log of frequency **(Figure 10)**. The nature of the plot shows that:
(i)   The dielectric loss is almost independent below140 and above 180 KHz.
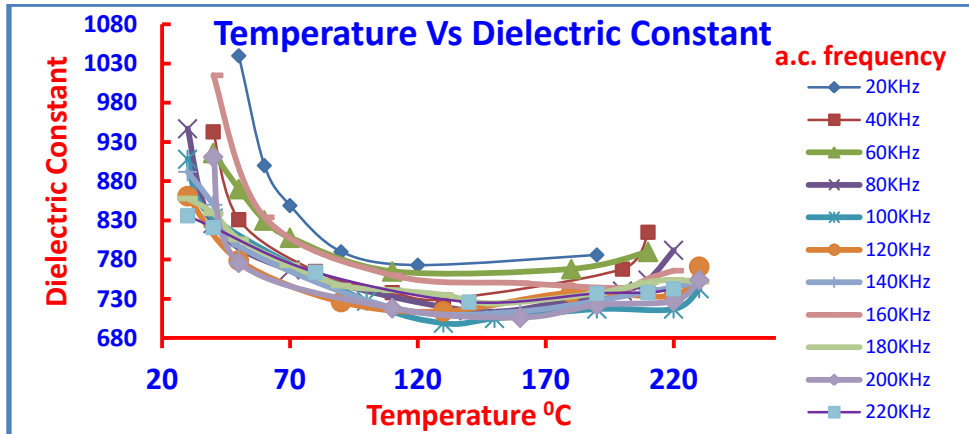(ii)   The maximum dielectric loss is observed at frequency nearly 160 KHz for all temperatures.

Figure 3: Graph of variation of dielectric constant with temperature for the frequency range 20KHz to 220KHz
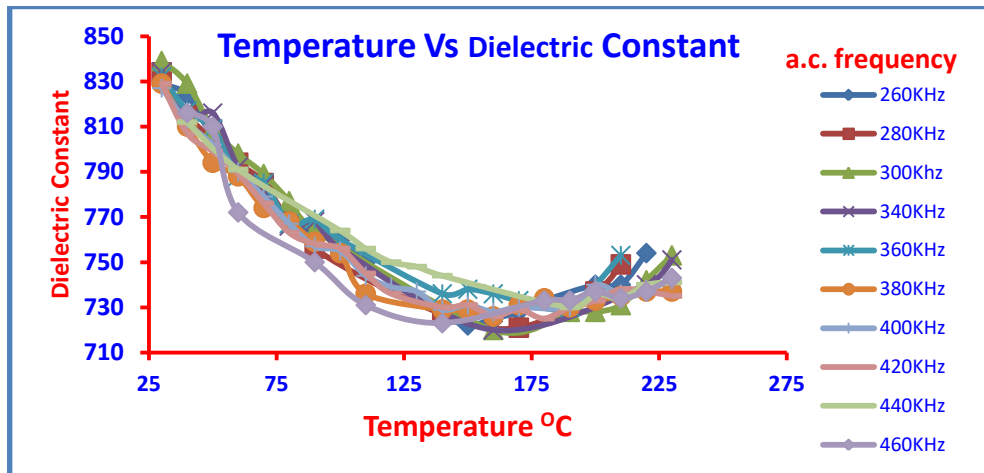
Figure 4: Graph of variation of dielectric constant with temperature for the frequency range 260KHz to 460KHz
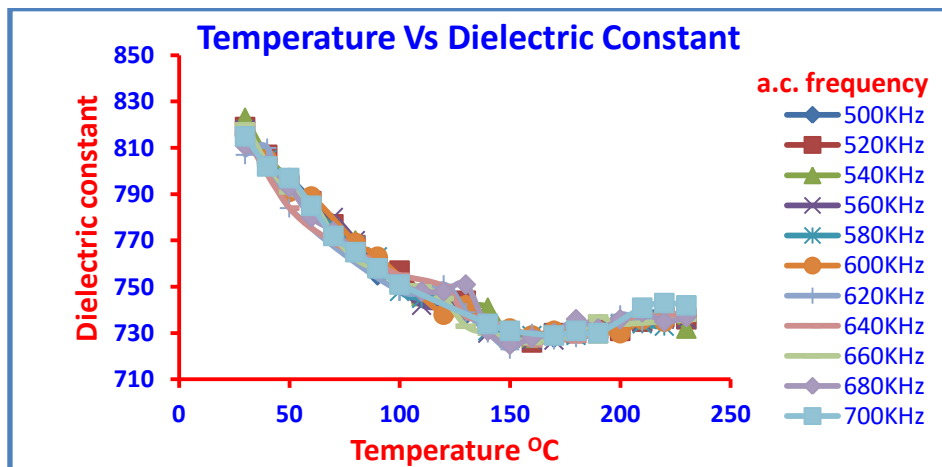
Figure 5: Graph of variation of dielectric constant with temperature for the frequency range 500KHz to 700KHz
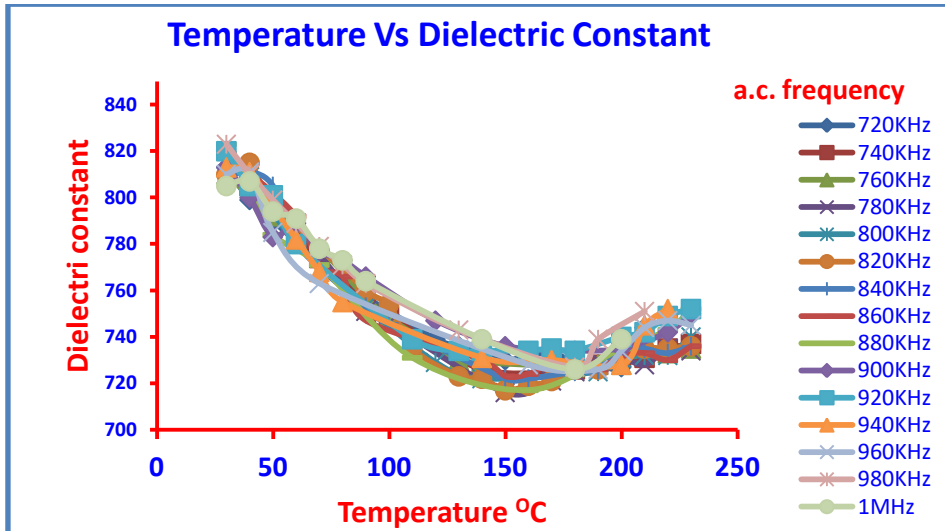
Figure 6: Graph of variation of dielectric constant with temperature for the frequency range 720KHz to 1MHz
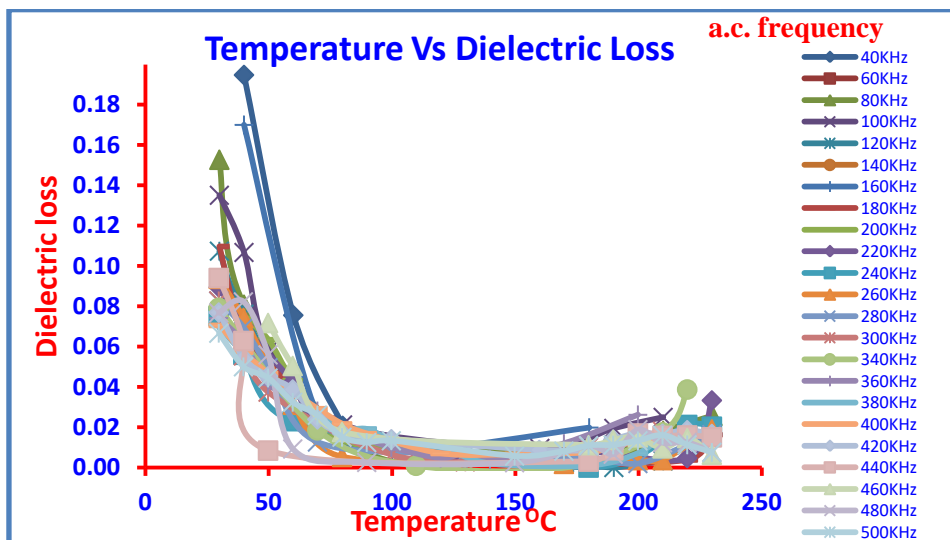

Figure 7: Graph of variation of dielectric loss with temperature for the frequency range 40KHz to 500KHz
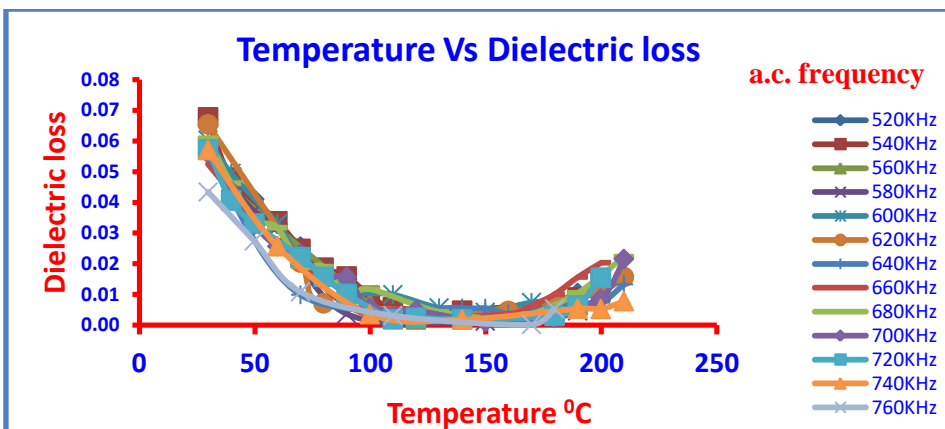

Figure 8: Graph of variation of dielectric loss with temperature for the constant frequency range 520KHz to 760KHz
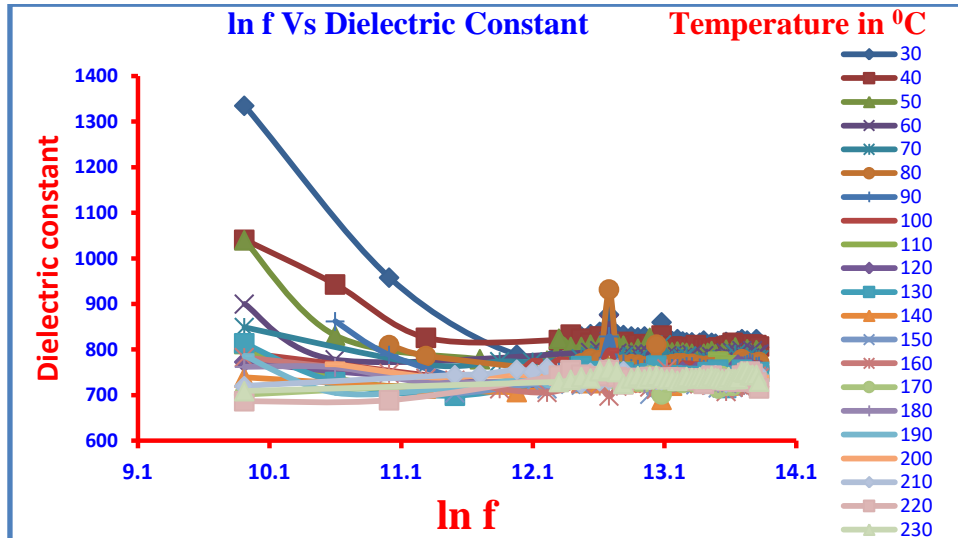
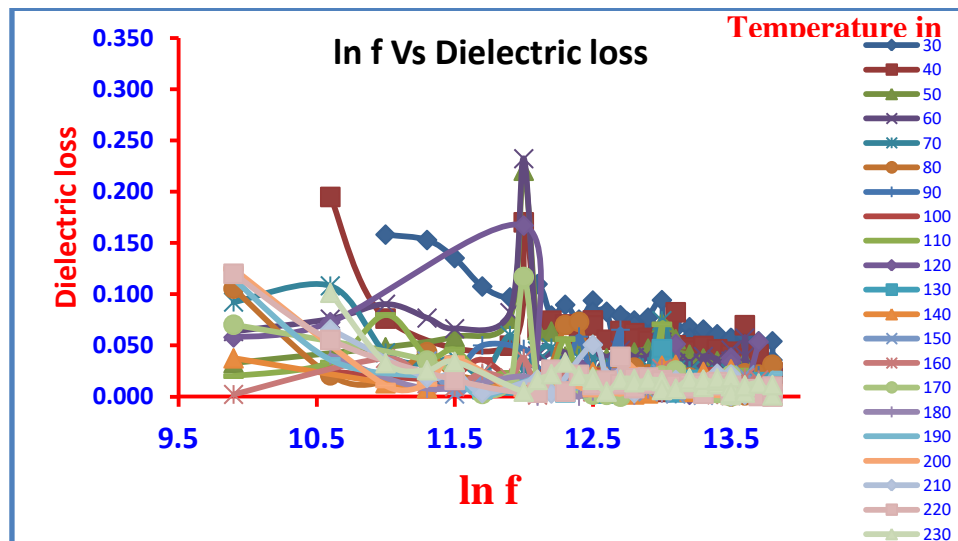**Figure 9:** Graph of variation of dielectric constant with frequency for the constant temperature range 30^0 to 230^0C

Figure 10: Graph of variation of dielectric loss with frequency for the temperature range 30^0 to 230^0C

The values of dielectric constant (**ε'**) and dielectric loss (**tanδ**) are sensitive to temperature as well as frequency. In the low temperature range 30^0 to 150^0C, **ε'**and **tanδ** are markedly decrease, whereas between 150^0 to 175 ^{0}C, these are essentially temperature independent. In the higher temperature region, i.e. beyond 175 ^{0}C, they become strongly temperature dependent, increasing faster with increasing temperature at constant applied frequencies. Evidently the material exhibits dielectric dispersion in this region.

Furthermore, dielectric constant decreases with increasing frequency upto nearly150 KHz and remain constant in higher frequency region.

The dielectric loss is maximum at about the frequency center to the lower and higher frequencies and almost minimum in lower and higher frequency region. Evidently, the dielectric dispersion in the material is again supported.

The dielectric constant of the dispersive medium in low temperature region is observed to be decreasing. This might be because the term contributing to dielectric constant resulting from ion-dipole interaction is compensated by thermal energy, leading to the relaxation of the polarization. In the temperature range 150^0 to 175 ^{0}C, **ε'** remains almost temperature independent, which indicate ion-core type of polarization in the material. Beyond 175^0C, the dielectric constant is found to increase with temperature. This may be ascribed to interfacial polarization mechanism. Faster increase of **ε'** as well as **tanδ** in the higher temperature region, the polarization increases because of the ease of accumulation of excess charge carries in the absence of ion-dipole contact. An ionic crystal with higher dielectric constant shows lower energy of formation lattice defect [28]. The defects can cause positive or negative space charge distribution which can move under application of an external

field and when they are trapped by the defects, larger numbers of dipoles are formed, giving rise to space charge polarization. Phonon generation at higher temperature is expected to rise ε' due to phonon drag. Phonon drag does not localized charge carriers, exhibiting atomic polarizability and physical expansion at lattice.

Now, **Figure 9** and **Figure 10** manifests that the dielectric constant and dielectric loss are both inversely proportional to frequency. This is normal dielectric behavior [29] that both **ε'** and **tanδ**   (**Figure 9** and **Figure 10**) decrease with increasing frequency.

At the low frequency side of **Figure 9**, the dielectric constant curve has its highest value. Here all of the polarizations have time to form and contribute their full amount to the dielectric constant. With increasing frequency, ε' begins to decrease as the relaxation frequency of the interfacial polarization is approached and reaches to a constant low value. Evidently, dielectric dispersion is noticeable at low frequency and low temperature[30].

At still higher frequencies, the dielectric constant **ε'** again decreases as the relaxation frequency of the dipole polarization is approached, and again reaches a constant lower value as the frequency becomes too high for the field to affect appreciably the orientation of dipoles.

It is observed from **Figure 10** that, dielectric loss minimum in lower frequency region. This low value of tanδ may be due to the dissipation of the energy of field as heat, because of the friction experienced by the bound charges or dipoles in their motion in the applied field in forming the polarizations. The theory of dispersion shows that the dielectric constant and dielectric loss are not independent quantities. Thus a material having a high dielectric constant must have a large dielectric loss at the frequency at which ε' has a value half way between its low and high frequency values. It is clearly seen in **Figure 10** at a frequency 180 KHz.

IV.   CONCLUSIONS

Dielectric constant (**ε'**) and dissipation factor (**tan δ**) of barium oxalate single crystals show similar trend of variation with frequency as well as temperature. A ferroelectric transition occurs near 30°C. As the temperature goes much beyond the transition temperature, dielectric dispersion becomes more evident. In the temperature range 150^0 to $175\ ^0$C dielectric constant is dominated to ion-core type of polarization. Beyond 175 °C, sharp increase of dielectric constant is due to space charge polarization, compatible with higher d.c. conductivity. Continuous fall of the dielectric constant with increasing frequency occurs because dipoles are not able to follow faithfully the impressed oscillating field.

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ULTRASONIC VELOCITY, DENSITY MEASUREMENTS OF （E）-2- HYDROXY -3- （4 - HYDROXY -5- ISOPROPYL -2- METHYL PHENYL）DIAZENYL）NAPTHALENE 1-4-DIONE IN MIXED SOLVENT AT 303.15 K

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ABSTRACT

The acoustical properties have been investigated from the ultrasonic velocity and density measurements of azo compound in 10% DMSO at 300.15K. The measurement have been perform to evaluate acoustical parameter such as adiabatic compressibility ($\square$s), Partial molal volume ($\square$v), intermolecular free length (Lf), apparent molal compressibility ($\square$k), specific acoustic impedance (Z), relative association (RA), solvation number (Sn).

KEYWORD: *Ultrasonic velocity, viscosity, adiabatic compressibility, apparent molal volume.*

INTRODUCTION

Azo compounds are a very important in the field of research. They are highly colored and have been used as dyes and pigments for a long time. In fact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts.[1, 2] In the recent years, measurements of the Ultrasonic velocity are helpful to interpreted solute-solvent, ion-solvent interaction in aqueous and non aqueous medium.[3-9] Fumio Kawaizumi[10] have been studied the acoustical properties of complex in water. Jahagirdar et. al. has studied the acoustical properties of four different drugs in methanol and he drawn conclusion from adiabatic compressibility. The four different drugs compress the solvent methanol to the same extent but it shows different solute-solvent interaction due to their different size, shape and structure.[11] Meshram et. al. studies the different acoustical properties of some substituted Pyrazolines in binary mixture acetone-water and observed variation of ultrasonic velocity with concentration.[12] Palani have investigated the measurement of ultrasonic velocity and density of amino acid in aqueous magnesium acetate at constant temperature.[13] The ion-dipole interaction mainly depends on ion size and polarity of solvent. The strength of ion-dipole attraction is directly proportional to the size of the ions, magnitude of dipole. But inversely proportional to the distance between ion and molecules. Voleisines has been studied the structural properties of solution of lanthanide salt by measuring ultrasonic velocity.[14] Syal et.al. has been studied the ultrasonic

velocity of PEG-8000, PEG- study of acoustical properties of substituted heterocyclic compounds under suitable condition.[15] Tadkalkar et.al. have studied the acoustical and thermodynamic properties of citric acid in water at different temperature.[16] Mishra et.al. have investigated ultrasonic velocity and density in non aqueous solution of metal complex and evaluate acoustic properties of metal complex.[17] M. Arvinthraj et.al. have determined the acoustic properties for the mixture of amines with amide in benzene at 303K-313K. They also determined thermodynamic parameters.[18] S.K. Thakur et.al. have studied the different acoustical parameters of binary mixture of 1-propanol and water.[19] Mirikar et.sal. studied the molecular interaction between liquids.[20]

After review of literature survey the detail study of azo cpomound under identical set of experimental condition is still lacking. It was thought of interest to study the acoustical properties of substituted heterocyclic drug under suitable condition.

Experimental

In the present study, the azo compound was used. The double distilled DMSO was used for preparation of different concentration of drug solution. The densities were determined by using specific gravity bottle by relative measurement method with accuracy $\square$ 1x10^{-5} gm/cm^{3}. The ultrasonic velocities were measured by using ultrasonic interferometer having frequency 3MHz. The constant temperature was maintained by circulating

water through the double wall measuring cell, made up of steel.

In the present investigation, different properties such as adiabatic compressibility ($\square$s), apparent molal volume ($\square_v$), intermolecular free length (L_f), apparent molal compressibility ($\square_\square$), specific acoustic impedance (Z), relative association (R_A), solvation number(S_n).

RESULTS AND DISCUSSION
In the present investigation, different acoustical properties such as ultrasonic velocity (Us), adiabatic compressibility ($\square$s), intermolecular free length (L_f), specific acoustic impedance (Z), are listed in table-1. Partial molal volume ($\square_v$), apparent molal compressibility ($\square_\square$), relative association (R_A), solvation number (Sn) are listed in table-2. It was found that the ultrasonic velocity decreased with the increase in concentration for system (Table-1). Variation of ultrasonic velocity in solution depends upon the increase or decrease of molecular free length after mixing the component. This is based on a model for sound propagation proposed by Eyring and Kincaud[13]. Intermolecular free length increased linearly on increase in concentration of azo compound in 10% DMSO. Hence, decreased in ultrasonic velocity with increase in concentration of drug. It happened because there was significant interaction between ions and solvent molecules suggesting a structure promoting behavior of the added electrolyte. The specific acoustic impedance (Z) increased with the decrease in concentration of azo

compound in 10% DMSO. When concentration of electrolyte was increased, the thickness of oppositely charged ionic atmosphere increases due to decrease in ionic strength. This is suggested by decrease in acoustic impedance with concentration in system. It was seen that the intermolecular free length increased with the increase in concentration in system. The intermolecular free length increased due to greater force of attraction between solute and solvent by forming hydrogen bonding. The adiabatic compressibility increased with the increase in concentration of solution. It happened due to collection of solvent molecule around ions, this supporting weak ion-solvent interaction. This indicates that there is significant solute-solvent interaction.

It was observed that apparent molal volume increased with concentration in system. It indicates the existence of strong ion-solvent interaction. It was found that the value of apparent adiabatic compressibility was increased with the increase in concentration of azo compound in DMSO. It shows strong electrostatic attractive force in the vicinity of ions. From the data, we were concluded that strong molecular association was found in azo compound. The value of relative association increased with the increase in concentration in system. It has been found that there was strong interaction between solute and solvent. There were regular increases in solvation number with the increase in concentration; it indicates the solvent molecule forms strong coordination bond in primary layer. It indicates the increase in size of secondary layer of Solvation.

Table 1: Ultrasonic velocity, density, adiabatic compressibility ($\square_S$), Specific acoustic impedance (Z) Intermolecular free length (L_f).

Concentration moles lit^{-1} (m)	Density (ds) kg m^{-3}	Ultrasonic velocity (Us) m s^{-1}	Adiabatic compressibiliy ($\square_S$) x10^{-10} m^{2}N^{-1}	Intermolecular free length (L_f) x10^{-11} m	Specific acoustic impedance (Zx10^6) kg m^{-2} s^{-1}
1x10^{-3}	1006.11	1431.48	3.40913	3.71346	1.4402
2x10^{-3}	1012.56	1443.87	3.32212	3.66577	1.4618
3x10^{-3}	1016.86	1458.44	3.22355	3.61097	1.4823
4x10^{-3}	1021.91	1471.72	3.13707	3.56221	1.5026
5x10^{-3}	1024.41	1487.21	3.04007	3.50670	1.5229
6x10^{-3}	1028.12	1499.37	2.96676	3.46416	1.5413
7x10^{-3}	1034.26	1519.65	2.84950	3.39502	1.5718
8x10^{-3}	1039.61	1536.54	2.75947	3.34095	1.5959
9x10^{-3}	1046.29	1559.23	2.63797	3.26657	1.6310

Table 2: Concentration (m), Relative association (R_A), Apparent molal compressibility ($\square_\square$), Apparent molal volume ($\square_v$), Solvation number (S_n).

Concentration(m) moles lit^{-1}	Apparent molal volume (-ϕ_v) m^{3}mole^{-1}	Apparent molar compressibility (ϕ_k)x10^{-10} m^2 N^{-1}	Relative association (R_A)	Solvation number (S_n)
1x10^{-3}	14.0338	1.1985	1.0491	0.67554
2x10^{-3}	9.3777	1.1676	1.0110	0.65811
3x10^{-3}	7.6777	1.1326	1.0095	0.63836
4x10^{-3}	6.8789	1.1018	1.0099	0.62103
5x10^{-3}	6.0094	1.0673	1.0076	0.60159
6x10^{-3}	5.5855	1.0413	1.0074	0.585910

7x10^{-3}	5.5473	0.9996	1.0065	0.56342
8x10^{-3}	5.3950	0.9676	1.0059	0.54539
9x10^{-3}	5.4760	0.9244	1.0052	0.52106

CONCLUSION

The present study shows the experimental data for ultrasonic velocity, density and viscosity at 300.15K for substituted heterocyclic azo compounds in 10% DMSO. From experimental data, the acoustical properties were calculated. The solute-solvent interaction and ion-ion / solute-solute interaction existing between compound and DMSO were also studied with the help of experimental data. Lastly it has been concluded from the experimental data, that the solute-solvent interaction in system are weak..

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Studies of Stability constant of Mixed Ligands with Transion metal Ions in Aqueous Medium at 303K.

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ABSTRACT

The interaction of transion metal ion with Mixed ligand (Ramipril+Lovastatin) drugs have been investigated by pH metric titration at 0.1 M ionic strength at room temperature in aqueous medium. The data obtained use to estimate the values of proton-ligand stability constant (P^k) and Metal -ligand stability constant (logK). It is observed that transition metal ion form 1:1, 1: 2 complexes with all the systems.

keyword: Formation Constant, ph Metry

I. INTRODUCTION

The studies of metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport f metal ion in the biological kingdom.

In the earlier papers extensive data base on metal complexes with substituted heterocyclic drugs was presented.

 Number of researchers[1-2] studied the Formation and Stability constant of metal complexes with transition metals. Mathieu W.A. Steenland et.al.[3] studies stability constant of Cu (II) and Ni (II) complexes of trans –dioxopentaaza macrocycles in aqueous solution by different technique. Hong-Wen Gaoet.al.[4] has studied the stability constant of Cu (II) and Co (II) complexes with CNBAC in water sample spectrophotometrically. Tuba Sismanoglu [5] have studied the stability constant of binary complexes of Nicotinamide with Mn (II) by pH metrically. He also determines change in free energy, change in enthalpy and change in entropy from stability constant at different temperature. Tekade et.al. [6] have been studied complex formation of Cu (II) and Co (II) metal ion complex with substituted isoxazolines. O.Yamauchi et.al.[7] studied stability constant of metal complexes amino acids with charged side chain by pH–metrically. Hayati Sari et.al.[8] studied the stability constant of glyoxime derivative and their Nickel, Copper, Cobalt and Zinc complexes potentiometric and theoretically.

After review of literature survey the detail study of complex under identical set of experimental condition is still lacking. It was thought of interest to study the chelating properties of substituted heterocyclic drugs under suitable condition with lanthanide by pH metrically.

II. MATERIAL AND METHOD

pH measurement were carried out with equip-tronic EQ-610 pH meter (accuracy $\pm$ 0.01 units) using combine glass electrode at room temperature. Metal ions solution were prepared in triply distill water and concentration estimated by standard method.[9] The solution of drug prepared in solvent .The pH metric reading in 30% ethanol

water mixture were converted to [H$^+$] value by applying the correction proposed by Van Uitert Haas.
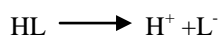
The overall ionic strength of solution was constant and calculated by the equation

$$\mu = 1/2 \ \Sigma \ C_i \ Z_i^2$$

The concentration of other ion in addition to   Na$^+$ and ClO$^-_4$ were also taken into consideration.

III. RESULT AND DISCUSSION

Substituted heterocyclic drugs may be ionized as acid having replaceable H$^+$ ion from -OH group. Therefore it is represented as HL i.e.

$$HL \longrightarrow H^+ + L^-$$

The titration data used to construct the curves between volume of NaOH and P^H. They are called acid-ligand titration curves.

It is observed from titration curves for all systems ligand start deviating from the free acid curves at P^H 2.5 and deviating continuously up to P^H =11. The deviation shows that dissociation of proton in substituted drugs.

The average number of proton associated with the ligand

(n$_A$) was determined from free acid and acid – ligand titration curves employing the equation of Irving and Rossotti[10] . The P^k values were determined from formation curves   (n$_A$ $_v^s$ P^H) by noting the P^H at which n$_A$ =0.5. The accurate values of pk were calculated by point wise calculations which are presented in table -1. The pK values are found.

Table-1 DETERMINATION OF PROTON-LIGAND STABILITY CONSTANT (pK) OF SOME SUBSTITUTED HETEROCYCLIC DRUGS AT 0.1M IONIC STRERNGTH.

System	Constant pK	
	Half integral	Point wise calculation
Ligand-1	5.70	5.680 ± 0.05

METAL -LIGAND STABILITY CONSTANT (Log k):-

Metal-ligand stability constant of transition metal ion chelate with drug were determined by employing Bjerrum calvin P^H metric titration method as adopted by Irving and Rossotti. The formation of chelate between transition metal ion with drug was indicated by the significant separation starting from pH =2.5 for transition metal ion with ligand -1.

Table-2 Determination of metal –ligand stability constant (logK) of transition metal ion WITH drugs at 0.1M ionic strength .

System	Logk$_1$	Logk$_2$	Logk$_1$ - Logk$_2$	Logk$_2$ / Logk$_1$
Cu(II)-Ligand	3.65	5.85	2.20	1.6027
Fe(II)-Ligand	3.80	5.76	1.96	1.5158
Ni(II)-Ligand	3.95	5.65	1.70	1.4303
Mg(II)-Ligand	4.05	5.95	1.90	1.4691
Co(II)-Ligand	4.35	6.30	1.95	1.4483

The result shows the ratio of $Logk_2/ Logk_1$ is positive in all cases. This implies that there is little or no steric hindrance to the addition of secondary ligand molecule .The smaller difference may be due to trans structure.

IV. ACKNOWLEDGEMENTS

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ULTRASONIC VELOCITY, DENSITY MEASUREMENT OF SCHIFF BASE OF (5-HYDROXY -3-METHYL-1-(2, 4-DINITROPHENYL) PYRAZOL-4-YL) (PHENYL) METHANONE AND ISONIAZIDE IN DIOXANE-WATER AT 303 K

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ABSTRACT

Using the ultrasonic velocity and density measurements of Schiff base of (5-hydroxy -3-methyl-1-(2,4dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and Isonicotic acid hydrazide (isoniazid) the acoustical properties have been studied in 10% 1, 4 dioxane at 300K. The acoustical parameter such as intermolecular free length (Lf), adiabatic compressibility ($\Box$s), Partial molal volume ($\Box$v), specific acoustic impedance (Z), apparent molal compressibility ($\Box$ k), relative association (RA), solvation number (Sn) have been evaluated and from the experimental data it is concluded that the interaction between solute and solvent in Schiff base of benzoyl Pyrazolone & dioxane systems are strong.

Keyword: - Apparent molal volume, Adiabatic compressibility, Schiff base, Ultrasonic velocity, Viscosity.

I. INTRODUCTION

In the modern research, interpretation of solute-solvent, ion-solvent interaction in non-aqueous and aqueous medium is done via measurements of the Ultrasonic velocity[1-5]. The acoustical properties of complex in water have been determined by F. Kawaizumi et.al[6]. The acoustical properties of four different drugs in methanol have been determined by Jahagirdar et.al[7]. And the conclusion was drawn by him from adiabatic compressibility. The solvent methanol compress by four different drugs to the same extent but their solute-solvent interaction is different due to the difference in their size, shape and structure[8]. The different acoustical properties of some substituted Pyrazolines in acetone-water binary mixture have been determined by Meshram et.al[9]. and he observed that the ultrasonic velocity vary with concentration. The ultrasonic velocity and density of amino acid in aqueous solution of magnesium acetate at constant temperature have been investigated by Palani et.al[10]. The ion-dipole interaction largely influenced by the size of ion and polarity of solvent. The strength of ion-dipole attraction is directly related to the ion size and magnitude of dipole but inversely related to the space between

molecules and ion. By measurement of ultrasonic velocity, the structural properties of solution of lanthanide salt have been studied by Voleisines et.al[11]. The ultrasonic velocity of PEG-8000 and substituted heterocyclic compounds under suitable condition have been determined by Syal et.al[12]. The thermodynamic and acoustical properties of citric acid in water at various temperatures have been studied by Tadkalkar et.al[13]. The acoustic properties, ultrasonic velocity and density of metal complex in non-aqueous solution are evaluate by Mishra et.al[14]. The thermodynamic parameters and acoustic properties for the solution of amide and amines in benzene have been determined by M. Arvinthraj et.al[15]. The different acoustical parameters of water and 1-propanol binary mixture have been studied by S.K. Thakur et.al[16]. The molecular interaction of liquids has been investigated by Mirikar et.al[17].The survey of literature show that, the detail study of Schiff base of Benzoyl Pyrazolone and Isonicotic acid hydrazide (isoniazid) under indistinguishable set of experimental circumstance is still lacking. It was thought of interest to study the acoustical properties of Schiff base of (5-hydroxy-3-methyl-1-(2,4dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and Isonicotic acid hydrazide (isoniazid) under appropriate condition.

II. EXPERIMENTAL

In the present study, the Schiff base of (5-hydroxy -3-methyl-1-(2,4dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and Isonicotic acid hydrazide (isoniazid) was used. Vogel's standard method use for purification of Dioxane[22]. The solution of different concentration of Schiff base was prepare in double distilled dioxane. The specific gravity bottle use to determine the densities by relative measurement method with accuracy $\pm$ 1x10^{-5} gm/cm^3. The ultrasonic interferometer having frequency 3MHz was used to determine the ultrasonic velocities. The temperature maintain constant by circulating water through the double wall measuring steel cell.

In the present analysis, different properties such as intermolecular free length (Lf), adiabatic compressibility (βs), apparent molal volume (ϕ_v), apparent molal compressibility (ϕ_κ),relative association (RA), specific acoustic impedance (Z), limiting apparent molal compressibility (ϕ^0_κ), limiting apparent molal volume(ϕ^0_v), solvation number(Sn) and their constant (S$_k$, S$_v$) have been evaluated.

III. THEORY

Adiabatic compressibility (βs) is calculated by using the relation

$$\beta s = \frac{1}{U^2_s d_s} \qquad (1)$$

Apparent molal compressibility (ϕ_κ) is determine by using the relation

$$(\phi_\kappa) = 1000 \times \left(\frac{\beta s\, d_0 - \beta 0\, d_s}{m \times ds \times d_0} \right) + \frac{\beta s \times M}{ds} \qquad (2)$$

Where $d_s, \beta s$ and $d_0, \beta 0$ are the density and adiabatic compressibility of solution and solvent respectively. m is concentration of solute in terms of molality and The molecular weight of solute is M .

$$\text{Apparent molal volume } (\phi_v) = \frac{M}{ds} \ x \ \frac{(d_0-ds) \ x 10^3}{mxdsxd_0} \tag{3}$$

$$\text{Specific acoustic impedance (Z)} = Us \ ds \tag{4}$$

$$\text{Intermolecular free length } (L_f) = K\sqrt{\beta}s \tag{5}$$

$$\text{Relative association } (R_A) = (ds / d_0) \ x \ (U_0 /U_s)^{1/3} \tag{6}$$

$$\phi_\kappa = \phi^0_\kappa + S_k C \tag{7}$$

$$\phi_v = \phi^0_v + S_V \ C \tag{8}$$

III. RESULTS AND DISCUSSION

In the present study, different acoustical properties such as Ultrasonic velocity (Us), adiabatic compressibility (β_S), Specific acoustic impedance (Z) and Intermolecular free length (L_f) are recorded in table-1. Solvation number (S_n), Relative association (R_A), Apparent molal volume (ϕ_v), Apparent molal compressibility (ϕ_κ) are recorded in table-2. Limiting Apparent molal compressibility (ϕ^0_κ), Limiting Apparent molal volume and their constant (S_k, S_v) are recorded in table-3. It was found that when concentration for system increase the ultrasonic velocity also increase (Table-1). Deviation of ultrasonic velocity in solution is depends on the decrease or increase of molecular free length after mixing the component. This is based on a model proposed by Eyring and Kincaud[13] for sound propagation. When concentration of Schiff base of benzoyl Pyrazolone in 10% 1, 4 dioxane increase Intermolecular free length(L_f) decrease linearly and hence increased in ultrasonic velocity observed with increase in concentration of Schiff base of benzoyl Pyrazolone. It was occurred due to strong interaction between solvent and ion molecules suggesting a structure promoting behavior of the added electrolyte. The specific acoustic impedance (Z) increased with the increase in concentration of Schiff base of benzoyl Pyrazolone in 10% dioxane. When concentration of electrolyte was increased, increase in ionic strength is observed hence the thickness of oppositely charged ionic atmosphere is decreases. This is suggested by increase in acoustic impedance with concentration in system. It was seen that when concentration in system increases the intermolecular free length is decreases. The intermolecular free length decreased due to greater force of attraction between solvent and solute molecule by creating hydrogen bonding. As the concentration of solution increases, the adiabatic compressibility is decreases. The decrease in to collection of solvent molecule around solute molecules indicates that there are solute-solvent interaction are presence. This indicates that there is strong interaction between solvent and solute molecule in solution and the solution is becoming more and more compressible.

It was observed that concentration in system is increases the apparent molal volume also increases. It indicates the existence of strong interaction between solvent and solute molecule. It was initiated that the value of apparent molal compressibility was decreased with the increase in concentration of Schiff base of benzoyl Pyrazolone in dioxane. It shows weak electrostatic attraction force between the close vicinity of ions. From the data, we were concluded that there are weak molecular association was found in Schiff base of benzoyl Pyrazolone. The value of relative association decreased as the concentration in system increases. It has been observed that there was weak interaction between solvent- solute. There was a decrease in solvation number as the concentration in system increases; it indicates the strong coordination bond forms by solvent molecule in primary layer. And due to this decrease in size of secondary layer of Solvation are observed. The value of S_k exhibits negative. It indicates the weak solute-solute or ion-ion interactions in Schiff base of benzoyl Pyrazolone system are present. From table-3, it was observed that the value of limiting apparent molal volume is positive. It indicates that the ion-dipolar interaction in Schiff base of benzoyl Pyrazolone and 1, 4 dioxane. The all value of Sv are positive, indicates the strong interaction between solvent and solute molecule. These value indicates an induced effect of 1, 4 dioxane on solvent- solute interaction. From fig. 1 and 2 the value of S_k and Sv has been determine.

Table-1 Density (ds), Ultrasonic velocity (Us), adiabatic compressibility (β_S),

Specific acoustic impedance (Z) and Intermolecular free length (L_f).

Concentration moles lit^{-1} (m)	Density (ds) Kg.m^{-3}	Ultrasonic velocity (Us) m.s^{-1}	Adiabatic compressibiliy (β_S)x10^{-10} m^{2}N^{-1}	Intermolecular free length (L_f)x10^{-11} m	Specific acoustic impedance (Zx10^6) kg m^{-2}.s^{-1}
Schiff base of benzoyl Pyrazolone + 10% 1,4 Dioxane					
1×10^{-3}	1019.86	1496	4.38240	4.2103	1.5255
2×10^{-3}	1019.96	1502	4.34356	4.19160	1.5324
3×10^{-3}	1020.05	1514	4.27801	4.15985	1.5442
4×10^{-3}	1020.13	1520	4.24396	4.14327	1.5504
5×10^{-3}	1020.21	1527	4.20371	4.12357	1.5579
6×10^{-3}	1020.28	1533	4.17058	4.10729	1.5641
7×10^{-3}	1020.35	1538	4.14430	4.09433	1.5691
8×10^{-3}	1020.41	1546	4.10233	4.07355	1.5771
9×10^{-3}	1020.47	1553	4.06100	4.05297	1.5852

Table-2 Concentration (m), Solvation number (S_n), Relative association (R_A), Apparent molal volume (ϕ_v) , Apparent molal compressibility (ϕ_κ).

Concentration (m) Moles.lit^{-1}	Apparent molal volume (ϕ_v) m^{3}mole^{-1}	Apparent molar compressibility (ϕ_k)x10^{-10} m^2 N^{-1}	Relative association (R_A)	Solvation number (S_n)

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1×10^{-3}	0.37215	2.09437	0.99789	0.98853
2×10^{-3}	0.37693	2.07553	0.99520	0.97964
3×10^{-3}	0.38170	2.04389	0.99153	0.96470
4×10^{-3}	0.38648	2.02739	0.98965	0.95692
5×10^{-3}	0.38933	2.00792	0.98739	0.94773
6×10^{-3}	0.39283	1.99189	0.98553	0.94016
7×10^{-3}	0.39532	1.97914	0.98406	0.93415
8×10^{-3}	0.39838	1.9589	0.98163	0.92459
9×10^{-3}	0.40076	1.93895	0.97922	0.91518

Table-3 Limiting Apparent molal compressibility (ϕ^0_κ), Limiting Apparent molal volume (ϕ^0_v), S_v and S_k

Ligand	Limiting Apparent molal volume (ϕ^0_v)m^{3}mole^{-1}	Limiting Apparent molal compressibility (ϕ^0_κ)x10^{-10} m^{2}N^{-1}	S_v m^{3}kg$^{1/2}$mole$^{-3/2}$	S_k m^{3}mole^{-2}kg.N^{-1}
Schiff base of benzoyl Pyrazolone	0.3705	2.1078	3.5397	-18.943
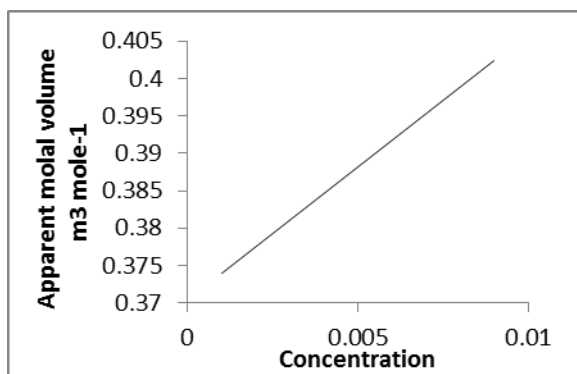
Fig.-1 -Apparent molal volume (m^3.mole^{-1}) Vs Concentration (mole.lit^{-1})
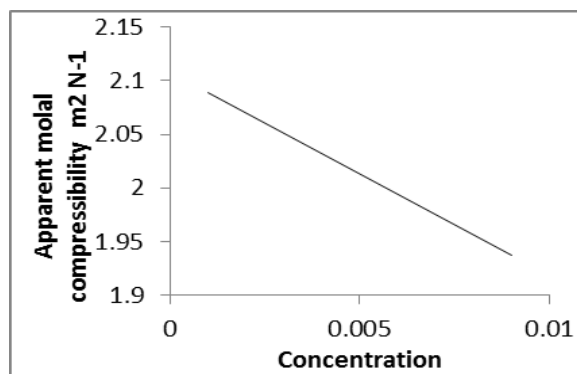
Fig.-2- Aparent molar compressibility10^{-9} (m^2.N^{-1}) Vs Concentration (mole.lit^{-1})

IV. CONCLUSION

The present study shows the experimental data for density, ultrasonic velocity and viscosity at 300K for Schiff base of (5-hydroxy -3-methyl-1-(2,4dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and Isonicotic acid hydrazide (isoniazid) in 10% 1,4 dioxane . The acoustical properties were calculated from experimental data. The interaction between solute-solute or ion-ion and solvent-solute exists between Schiff base of benzoyl Pyrazolone and 1,4dioxane were also studied with the help of experimental data. Lastly from the experimental

data it is concluded that the interaction between solute and solvent in Schiff base of benzoyl Pyrazolone & dioxane systems are strong.

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Fuzzy Rule Based System to Characterize the Decision Making Process in Share Market

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ABSTRACT: Investors are not always completely rational and they do not always work only with numbers. Sometimes, they use linguistic concepts to make their decisions. Fuzzy logic is helpful in handling such situations. This research proposes an innovative method for forecasting stock. The proposed stock forecasting method is a combination of Technical Analysis, Fuzzy logic. one of the most important issues for investors in stock market. In this paper, a fuzzy approach to stock market timing is investigated. A fuzzy decision system is constructed based on experiences and techniques of stock and future opportunist. The success of the system is measured by comparing system output versus stock price movement.

KEYWORDS: Fuzzy logic, timing, share stock market, Forecasting, Trading.

I. INTRODUCTION

"Few human activities have been so exhaustively studied during the past fifty years, from so many angles and by so many different sorts of people, as has the buying and selling corporation securities. The rewards which the stock market holds out to those who read it right are normous; the penalties it exacts from careless, dozing or 'unlucky' investors are calamitous - no wonder it has attracted some of the world's most astute accountants, analysts and researchers" [1]. Forecasting the stock price and determining the market timing, when to buy and sell stocks, are the two main problems which most researchers and practitioners face in order to get high
financial gain.

There are two main approaches to predict stock prices, namely fundamental analysis and technical analysis. Fundamental analysis is a method of forecasting the future price movement of a financial instrument which is based on examining the company's financials and operations such as sales, earnings, growth potential, assets, debt, management, products, and competition, macroeconomic data, politics, environment and other relevant factors. Technical analysis involves using past stock prices, volume, and other related data to forecast the future price movements [2].
Several techniques have been researched to predict the stock price and produce trading signals in order to determine when to buy and sell stocks.

The objective type fuzzy modeling has excellent learning capabilities and requires less computational effort. Subtractive clustering technique used operates on raw numerical data. Increasing the number of inputs affects the prediction system only to a small extent. Further this clustering technique provides similar degree of accuracy and robustness together with lesser computational complexity as compared to various other clustering techniques. These advantages along with the characteristic that no separate defuzzification is required, makes this
prediction faster than several previous systems.

This study explores the possibility of applying fuzzy logic theory for handling vagueness and imprecision that characterize the decision making process. Fuzzy Logic framework is developed to carry out the required analysis for arriving at the governance rating of the firms. This research work will help the customer for decision making in share market A person carrying a share of a company holds that part of ownership in that company. Share is nothing but the Ownership of the company divided into small parts and each part is called as Share or Stock. Buy-Back is a corporate action in which a company buys back its shares from the existing shareholders usually at a price higher than market

price. When it buys back, the number of shares outstanding in the market reduces and hence the market capitalization as per below relation:

Market capitalization = Market value * Number of shares outstand

Companies also go for buyback with intent of projecting better financial ratios as indicated below:

Earnings per share(EPS) = Earnings/ Shares out- standing

Since outstanding shares reduce, the company's earnings are now divided amongst less number of shares for calculating EPS value. From investor's point of view, higher the earnings per share, better it is as an investment option. Share market is the place where buying and selling of shares takes place. The buying and selling of shares takes place from anywhere wherever with the help of internet connected computer.

One should need the demat account, computer and internet connection and he/she can start the share trading or investing. When you place the buy order, the message is transferred to the exchange [either NSE {National Stock Exchange} or BSE {Bombay Stock Exchange}] and the order stays in the queue of exchange's other orders and gets executed if the price of that share comes to that value. Once you get the confirmation of this transaction, the shares purchased, will be sent to your demat account. The shares will be stored in demat account in electronic format. The Sensex is an "index". An index is basically an indicator. It gives you a general idea
about whether most of the stocks have gone up or most of the stocks have gone down. In India the Sensex is an indicator of all the major companies of the BSE and the Nifty is an indicator of all the major companies of the NSE. If the Sensex goes up, it means that the prices of the stocks of most of the major companies on the BSE have gone up. If the Sensex goes down, this tells you that the stock price of most of the major stocks on the BSE have gonedown. The Sensex represents the top stocks of the BSE and the Nifty represents the top stocks of the NSE. Besides Sensex and the Nifty there are many other indexes Many different types of investors hold the shares of a company. Fig.1 shows BSE and NSE data.
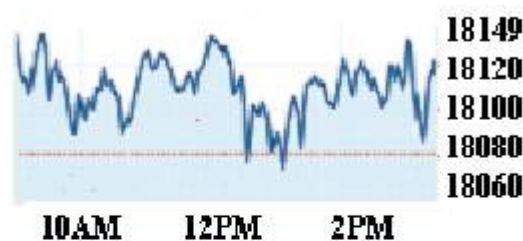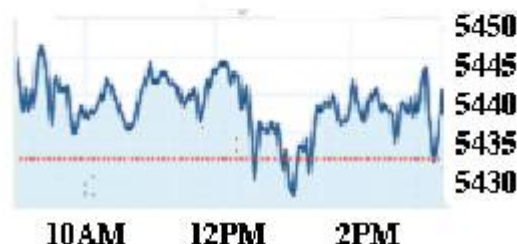
II. LITERATURE SURVEY

Predictability of financial time series can be viewed in two different ways: forecasting by level (value) estimation models and forecasting by classification models. The first method relies on accurate prediction of the price level of stocks, indices, and other financial series instruments. (e.g., see Teixeira & Rodrigues, 1997; Chakraborty, 2006; Dutta *et al.*, 2006; Panda & Narasimhan, 2006; Sohn & Lim, 2007; Majhi *et al.*, 2009; Mostafa, 2009; Chen, Hsin & Wu, 2010, Shen *et al.*, 2011). The degree of accuracy and the acceptability of the forecast are measured by its deviation from the actual observations, thus minimizing forecasting errors. The second method is guided by forecasts on the direction/sign of the changes in price levels.

This latter approach is defended by some authors (e.g., see Wu & Zhang, 1997; Aggarwal & Demaskey, 1997; Tsaih, Hsu & Lai, 1998; Leung, Daouk & Chen, 2000; Chen, Leung & Daouk, 2003; Kim, Min & Han, 2006; Faria *et al.*, 2009; Lu, 2010; Na & Sohn, 2011), who claim that trading driven by a certain forecast with a small forecast error may not be as profitable as trading based on an accurate prediction of the direction/sign of the movement. At the same time, several researches in the area of business have used fuzzy logic to handle imprecise information and improved results.

Some of them are Shehab & Abdalla (2002) and Murcia, Borba, & Souto-Maior (2005) in a costing system; Sahin & Dogan (2003) in supplies and customers relationship; Jiang & Hsu (2003) in manufacturing and business cycle evaluations; Lin, Hwang, Becker (2003) in accounting frauds detection; Beynon, Peel, & Tang (2004) in price composition of auditing services; Wang & Hsu (2008) in tourism demand; Keles, Kolcak, & Keles (2008) in domestic debt; Wang, Chang, & Tzeng (2011) and Wu (2010, 2011) in automobile sales; and Cheng, Tsai, & Sudjono (2010) in project cash flow control.

In the area of finance, works related to stock selection (such as Tanaka & Guo, 1999; Inuiguchi & Tanino, 2000; León, Liern & Vercher, 2002; Wang & Zhu, 2002; Serguieva & Hunter, 2004; Tiryaki & Ahlatcioglu, 2009), option pricing (Thavaneswaran, Appadoo & Paseka, 2009), and insolvency prediction (Tseng & Lin, 2005; Vigier & Terceño, 2008; Chen, Huang & Lin, 2009) have also used fuzzy logic.

III. OBJECTIVES

- To develop an algorithm based on technical analysis and neural fuzzy network to apply to forecasting and trading stock.
- To evaluate the efficiency of the developed algorithm.
- To map many different financial indicators into new inputs that can be "fuzzified". Use fundamental indicators with fuzzy logic to set up long-term investment plans and use technical indicators with fuzzy
- Logic to set up short-term investment plans.
- To create membership functions; to associate between inputs and outputs via fuzzy rules.
- To translate the fuzzy output into a crisp trading recommendations.

Utilization of the Study
The research has benefits as follow:
- To help traders and investors in forecasting the stock price and determining the market timing.
- To investigate the effect of using technical analysis and neural fuzzy network to forecasting and trading stocks.

IV. PROPOSED METHODOLOGY AND DISCUSSION:

Algorithm:
A. D**ecision tree:** A **decision tree** is a structure that includes a root node, branches, and leaf nodes. Each internal node denotes a test on an attribute, each branch denotes the outcome of a test, and each leaf node holds a class label. The topmost node in the **tree** is the root node. Mining big data is the process of extracting knowledge to uncover large hidden information from the massive amount of complex data or databases

DT induction is a top down recursive divide and conquer algorithm for multi-class classification task (Han et al., 2011). It is easy to interpret and explain, also requires little prior knowledge. Nonlinear relationships between features do not affect the tree performance. The goal of DT is to iteratively partition the data into smaller subsets until all the subsets belong to a single class or the stopping criteria of DT building process are met. During the early 1980s, Quinlan (1986) proposed ID3 (Iterative Dichotomiser 3) algorithm that used information theory to select the best feature, A j. The Aj with the maximum Information Gain is chosen as root node of the tree.

```
Input:
D = {x₁, ..., xᵢ, ..., x_N}, training data set;
k, number of iterations;
DT learning scheme;
Output: rule-set; // A set of classification rules.
Method:
 1: rule-set = ∅;
 2: for i = 1 to N do
 3:     xᵢ = 1/N; // initialising weights of each xᵢ ∈ D.
 4: end for
 5: for j = 1 to k do
 6:     if j==1 then
 7:         create Dⱼ, by sampling D with replacement;
 8:     else
 9:         create Dⱼ, by Dⱼ₋₁ and D with maximum weighted X;
10:     end if
11:     build a tree, DTⱼ ← Dⱼ by randomly selected features;
12:     compute error(DTⱼ); // the error rate of DTⱼ.
13:     if error(DTⱼ) ≥ threshold-value then
14:         go back to step 6 and try again;
15:     else
16:         rules ← DTⱼ; // extracting the rules from DTⱼ.
17:     end if
18:     for each xᵢ ∈ Dⱼ that was correctly classified do
19:         multiply the weight of xᵢ by (error(DTⱼ)/(1-error(DTⱼ))); // update
            weights.
20:     end for
21:     normalise the weight of each xᵢ ∈ Dⱼ;
22:     rule-set = rule-set ∪ rules;
23: end for
24: return rule-set;
25: create sub-data set, D_misclassified with misclassified instances
    from Dⱼ;
26: analyse D_misclassified employing algorithm 4.
```

B. Naive Bayes classifiers :

Naive Bayes classifiers can handle an arbitrary number of independent variables whether continuous or categorical. Given a set of variables, $X = \{x1, x2, x..., xd\}$, we want to construct the posterior probability for the event Cj among a set of possible outcomes $C = \{c1, c2, c..., cd\}$. In a more familiar language, X is the predictors and C is the set of categorical levels present in the dependent variable. Using Bayes' rule:

$$p\left(C_j \mid x_1, x_2, \dots, x_d\right) \propto p\left(x_1, x_2, \dots, x_d \mid C_j\right) p\left(C_j\right)$$

where $p(C_j \mid x_1, x_2, x \dots, x_d)$ is the posterior probability of class membership, i.e., the probability that X belongs to C_j. Since Naive Bayes assumes that the conditional probabilities of the independent variables are statistically independent we can decompose the likelihood to a product of terms: and rewrite the posterior as:

$$p\left(C_j \mid X\right) \propto p\left(C_j\right) \prod_{k=1}^{d} p\left(x_k \mid C_j\right)$$

Using Bayes' rule above, we label a new case X with a class level C_j that achieves the highest posterior probability.

The Naive Bayes Classifier technique is based on the so-called Bayesian theorem and is particularly suited when the dimensionality of the inputs is high. Despite its simplicity, Naive Bayes can often outperform more sophisticated classification methods.
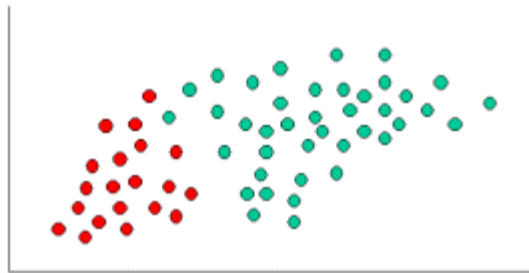
To demonstrate the concept of Naïve Bayes Classification, consider the example displayed in the illustration above. As indicated, the objects can be classified as either GREEN or RED. Our task is to classify new cases as they arrive, i.e., decide to which class label they belong, based on the currently exiting objects.

Since there are twice as many GREEN objects as RED, it is reasonable to believe that a new case (which hasn't been observed yet) is twice as likely to have membership GREEN rather than RED. In the Bayesian analysis, this belief is known as the prior probability. Prior probabilities are based on previous experience, in this case the percentage of GREEN and RED objects, and often used to predict outcomes before they actually happen.

Thus, we can write:

$$Prior\ probability\ for\ GREEN \propto \frac{Number\ of\ GREEN\ objects}{Total\ number\ of\ objects}$$

$$Prior\ probability\ for\ RED \propto \frac{Number\ of\ RED\ objects}{Total\ number\ of\ objects}$$

C. Importance of methodology:
- As stock market data are highly time-variant and are usually in a nonlinear pattern, predicting the future trend (i.e., rise, decrease, or remain steady) of a stock is a challenging problem.
- Uncovering market trends, planning investment strategies, identifying the best time to purchase the stocks and what stocks to purchase are included in stock market. For approaching these enormously complex and dynamic problems with data mining tools with help of fuzzy approach.
- By using fuzzy clustering technique, the whole training set can be divided into subsets which have less size and lower complexity.
- Objective fuzzy modelling used to build the prediction system requires numerical inputs. The IF-THEN rules formed have vague predicates in their antecedent part while the consequent part is a linear or quadratic combination of the antecedent variables. Since the consequent parts of rules are crisp values rather than vague

and fuzzy ones, there is no need to defuzzify the output. This characteristic of the objective fuzzy modeling technique favours it over several other fuzzy modeling techniques and is utilized to improve the prediction efficiency.

- The objective type fuzzy modelling has excellent learning capabilities and requires less computational effort.

D. There are six main factors which affect the share market :

I. **Market growth:** A fast growing market is generally considered attractive, and pulls a lot of
organisation's resources in an effort to increase gains. A case in point is the technological market widely consider by experts as a fast growing market, and tends to attract a lot of competition. The strength of this growth in the stock market has been corporate earnings. When a company says there is "strong market growth", they mean that the overall demand for the product they are selling has increased. The positive market growth has also improved the
overall standard of living of the people in the country. India market growth looks optimistic and
bright in the recent years to come. The service sector contributes around 54% of the annual Gross Domestic Product while the share of the industrial and agricultural sectors is 29% and 17% respectively. India is steadily becoming one of the global business giants with its booming market scenario.

II. **Monsoon:** The "monsoon effect" does have an impact on demand for fertilizers and tractors, and to a lesser extent, two-wheelers and consumer durables. The spatial distribution of the monsoon appears to wield a greater influence on sales growth rates, than does the absolute quantum of rainfall in a year. About 60% of Indian Agriculture is monsoon dependent. With rainfall this time being deficient by 45%, the agriculture sector has been hit hard. If monsoon showing no sign of rain, the rural income is bound to decrease, this eventually will affect the organization's plans and economic conditions. If the monsoon situation does not improve, it could result in downgrading of GDP growth estimates, downgrading corporate earnings estimates, a fall in the premium given to Indian markets and a consequent fall in Indices and stock market.

III. **Policy/ Political Impact:** After independence the development of India's economy was based on socialist-inspired policies. These policies like "Licence Raj" and others to protect from the world markets. The political Economy of India is rapidly changed with the liberalization of the economy in the 1990's. It has now moved towards a market based system and is the world's second fastest growing major economy after China. India recorded the highest GDP growth rate of 9% in2007. SEBI, the country's stock market regulator: Only eight stock exchanges enjoy "permanent" recognition from the Securities and Exchange Board of India (SEBI) out of a total of 24 equity bourses in the country. These "permanent" bourses include Bombay Stock Exchange (BSE) and National Stock Exchange (NSE) -- the two stock exchanges synonymous with
the Indian equity market. Other bourses that have been granted 'permanent' status by the regulator include Ahmadabad Stock Exchange, Bangalore Stock Exchange, Calcutta Stock Exchange, Madhya Pradesh Stock Exchange, Madras Stock Exchange and Delhi Stock Exchange(DSE). While presenting the Budget for 1992-93, the Finance Minister had announced a decision to allow reputed foreign investors, such as Pension Funds etc., to invest in India capital market. To operationalise this policy announcement, it has become necessary to evolve guidelines for such investments by Foreign Institutional Investors (FIIs). For granting registration
to the FII, SEBI shall take into account the track record of the FII, its professional competence,
financial soundness, experience and such other criteria that may be considered by SEBI to be
relevant. Besides , FII seeking initial registration with SEBI shall be required to hold a registration from the Securities Commission, or the regulatory organization for the stock market in the country of domicile/incorporation of the FII.

IV. **Foreign Investment:** The entry of more foreign investors into emerging markets may lead to pressure to upgrade trading systems and modify legal systems to support more trading and the introduction of a greater variety of financial instruments. The removal of barriers to foreign investment can improve the operation of domestic capital markets.

V. **Ratio Analysis** : Ratio Analysis is the hart of financial analysis,which shows the economic

condition of business.The aim of ratio analysis is to find out relative study, conciseness, and analysis of business activities. Financial ratio are useful because they summarise briefly the results of detailed and complicated computationsfor a cmpany . On the basis of purpose the financial ratio has four major types. Liquidity Ratio,Leverage Ratios, Activities Ratios, Portfitability Ratios.

VI. **Agent activities:** Indian stock exchange allows a member broker/agent to perform some activities. Act as an agent to Buy or Sell share/securities for their clients and charge commission for the same.

E. FUZZY CONTROLLER
Figure 3 gives the structure of a fuzzy controller, which is essentially the structure of a Mamdani technical fuzzy controller. Trend in prices information is the Crisp input which is fuzzyficated to mapped on fuzzy sets. We evaluate stock price and the trend in prices over some period of time and then decide whether to trade based on simple rules. The result is in each case a real number in the interval [01].
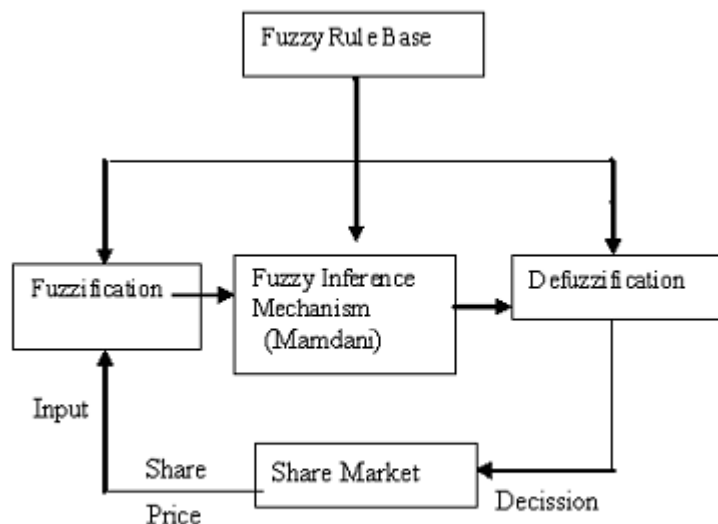

Fig.3 Fuzzy Controller

A. Fuzzy Rules
Rule1:- If (market_ growth is low) and (monsoon is low) and (policy_ and_ political impact is low) and (foreign_investment is low) and (ratio_ analysis is low) and (agent_ activities is low) then (Decision is hold).

Rule2:-
If (market_ growth is medium) and (monsoon is medium) and (policy_ and_ political impact is low) and (foreign_ investment is low) and (ratio_ analysis is medium) and (agent_ activities is low) then (Decision is hold).

Rule3:-
If (market_ growth is medium) and (monsoon is high) and (policy_ and_ political impact is high) and (foreign_ investment is low) and (ratio_ analysis is medium) and (agent_ activities is medium) then (Decision is purchase).

Rule4:-
If (market_ growth is high) and (monsoon is high) and (policy_ and_ political impact is high) and (foreign_ investment is high) and (ratio_ analysis is medium) and (agent_ activities is medium) then (Decision is purchase).

Rule5:-
If (market_ growth is high) and (monsoon is medium) and (policy_ and_ political impact is high)
and (foreign_ investment is medium) and (ratio_ analysis is high) and (agent_ activities is medium) then (Decision is purchase).

Rule6:-
If (market_ growth is high) and (monsoon is low) and (policy_ and_ political impact is high) and (foreign_investment is high) and (ratio_ analysis is high) and (agent_ activities is high) then (Decision is purchase).

Rule7:-
If (market_ growth is high) and (monsoon is medium) and (policy_ and_ political impact is
medium) and (foreign_ investment is medium) and (ratio_ analysis is medium) and (agent_ activities is high) then (Decision is purchase).

Rule8:-
If (market_ growth is medium) and (monsoon is high) and (policy_ and_ political impact is high) and (foreign_ investment is high) and (ratio_ analysis is high) and (agent_ activities is high) then (Decision is purchase).

Rule9:-
If (market_ growth is low) and (monsoon is low) and (policy_ and_ political impact is low) and (foreign_ investment is low) and (ratio_ analysis is medium) and (agent_ activities is medium) then (Decision is sell).

Rule10:-
If (market_ growth is low) and (monsoon is medium) and (policy_ and_ political impact is medium) and (foreign_ investment is high) and (ratio_ analysis is high) and (agent_ activities is high) then (Decision is sell).

Rule11:-
If (market_ growth is high) and (monsoon is medium) and (policy_ and_ political impact is high)
and (foreign_ investment is high) and (ratio_ analysis is high) and (agent_ activities is high) then (Decision is purchase).

Rule12:-
If (market_ growth is high) and (monsoon is low) and (policy_ and_ political impact is high) and (foreign_investment is high) and (ratio_ analysis is medium) and (agent_ activities is medium) then (Decision is purchase).

Rule13:-
If (market_ growth is low) and (monsoon is low) and (policy_ and_ political impact is medium) and (foreign_ investment is medium) and (ratio_ analysis is mrdium) and (agent_ activities is medium) then (Decision is hold).

V. SYSTEM EVALUATION

Any investment always involves a tradeo: between risk and reward. The higher the reward an investor seeks, the greater the risks and uncertainties are likely to be. Over any given period, stock prices will 5uctuate widely in response to company news, changes in industry conditions, the overall economics and potential climate, unexpected events, and shifts in investor psychology.

The proposed fuzzy logic system was used on the following dataset. Historical data for Stocks and Corporate Data can be provided as standard products, i.e. without filtering for user selected data points, or on customized basis.

The data used in simulation is daily closing prices and daily exchange volumes of stocks. The basic information of these stocks, including stock code, name, number of samples (one day for one sample) and the first day, are listed in Table II. The last day of the simulation period, 2017-Mar-06, is the same for all the sample stocks.

We are considering different following fields for Fuzzy Rule Based System to Characterize the Decision Making Process in Share Market.

Sr No	Fields (Values)
1	SERIES
2	OPEN
3	HIGH
4	LOW
5	CLOSE
6	LAST
7	PREVCLOSE
8	TOTTRDQTY
9	TOTTRDVAL
10	TIMESTAMP
11	TOTALTRADES
12	ISIN

We are using sample training dataset of stock exchange. Here we are using dataset of 06 Mar 2017.

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	SYMBOL	SERIES	OPEN	HIGH	LOW	CLOSE	LAST	PREVCLOSE	TOTTRDQTY	TOTTRDVAL	TIMESTAMP	TOTALTRADES	ISIN
2	20MICRONS	EQ	36.3	36.85	36	36.45	36.15	36	37322	1361829.65	6-Mar-17	188	INE144J01027
3	3IINFOTECH	EQ	5.2	5.25	5.15	5.2	5.2	5.1	1168403	6071872.05	6-Mar-17	456	INE748C01020
4	3MINDIA	EQ	11028.25	11090	10705	10919.65	10974.95	10919.1	802	8792593.25	6-Mar-17	343	INE470A01017
5	63MOONS	EQ	78.7	79.65	78.55	78.9	78.95	78.95	33224	2624059.95	6-Mar-17	931	INE111B01023
6	8KMILES	EQ	619	631	610.1	614.7	615	620.9	66292	41124915.65	6-Mar-17	3590	INE650K01021
7	A2ZINFRA	EQ	41.7	42	40.35	40.9	40.75	41.7	520277	21497292.1	6-Mar-17	3150	INE619I01012
8	AARTIDRUGS	EQ	591.4	591.45	580.9	583.6	581.15	582	4240	2487878.85	6-Mar-17	539	INE767A01016
9	AARTIIND	EQ	744	751.9	717.1	734	744.2	741.75	35665	26405140.75	6-Mar-17	2752	INE769A01020
10	AARVEEDEN	EQ	75.7	75.9	71.5	74.1	73.85	74.4	8606	634884.2	6-Mar-17	135	INE273D01019
11	ABAN	EQ	231.35	234.25	230.75	232.15	232.7	230.95	494408	114850541.6	6-Mar-17	7199	INE421A01028
12	ABB	EQ	1230	1237.95	1192.55	1200.4	1200	1228.4	26793	32454755.8	6-Mar-17	2977	INE117A01022
13	ABBOTINDIA	EQ	4499	4499	4456	4490.5	4492	4476.25	1961	8801915.3	6-Mar-17	437	INE358A01014
14	ABFRL	EQ	154.45	155	149.9	150.8	150.3	153.75	350731	53413208.25	6-Mar-17	9119	INE647O01011
15	ABGSHIP	BZ	24.3	25	24.25	24.25	24.25	25.5	46551	1130854.35	6-Mar-17	192	INE067H01016
16	ABIRLANUVO	EQ	1487	1492.7	1455.2	1463.7	1461.1	1485.65	164353	241136849.6	6-Mar-17	6771	INE069A01017
17	ABMINTLTD	BE	173	173	167.5	167.5	167.5	165	200	33917	6-Mar-17	9	INE251C01017
18	ACC	EQ	1398	1407.4	1388.55	1393.45	1394.8	1393.7	151011	210813694.1	6-Mar-17	8289	INE012A01025
19	ACCELYA	EQ	1500	1525	1453.9	1462.5	1461	1489.85	1902	2819479.5	6-Mar-17	564	INE793A01012
20	ACE	EQ	54.75	55.5	54.4	54.95	55.05	54.4	189485	10422950.65	6-Mar-17	867	INE731H01025
21	ACROPETAL	BZ	1.65	1.65	1.65	1.65	1.65	1.6	13442	22179.3	6-Mar-17	10	INE055L01013
22	ADANIENT	EQ	95.05	95.85	94.05	95.4	95.2	94.7	2240085	213018926.5	6-Mar-17	9251	INE423A01024
23	ADANIPORTS	EQ	297.85	304.9	296.45	303.15	304	296.35	1877927	564294453.4	6-Mar-17	29453	INE742F01042
24	ADANIPOWER	EQ	37.1	38.9	36.9	38.55	38.85	37.05	6301171	238759350.7	6-Mar-17	10657	INE814H01011
25	ADANITRANS	EQ	63.45	63.45	62.05	62.35	62.25	62.55	729958	45701730.2	6-Mar-17	4593	INE931S01010

26	ADFFOODS	EQ	164.2	171.4	164.05	168.1	167.5	152.4	873568	146397828	6-Mar-17	11637	INE982B01019
27	ADHUNIK	EQ	7.65	7.85	7.55	7.7	7.8	7.6	70090	542029.6	6-Mar-17	583	INE400H01019
28	ADHUNIKIND	EQ	104.8	112.1	103.4	105.95	105	108.05	33302	3560024.2	6-Mar-17	276	INE452L01012
29	ADLABS	EQ	81.5	85	80.8	83.55	83.55	80.75	524412	43679213.1	6-Mar-17	4315	INE172N01012
30	ADORWELD	EQ	299.95	300.1	297	297.25	297	298.95	3587	1069901.75	6-Mar-17	143	INE045A01017
31	ADSL	BE	30	30.95	29.65	30	30.25	30.45	25646	771641.05	6-Mar-17	116	INE102I01027
32	ADVANIHOTR	EQ	52.1	52.9	51.6	51.85	51.6	51.7	2440	127561.1	6-Mar-17	37	INE199C01026
33	ADVENZYMES	EQ	1722	1722	1677	1686.55	1693.05	1711.95	43861	74359056.15	6-Mar-17	3373	INE837H01012
34	AEGISCHEM	EQ	195.85	200	195.5	198.6	197.1	194.2	218243	43055837.8	6-Mar-17	2501	INE208C01025
35	AFL	EQ	75.85	77.65	72.2	72.5	72.7	77.1	180039	13387210.9	6-Mar-17	2184	INE020G01017
36	AGARIND	EQ	504.4	512	495	503	500	499.55	91186	45818107.5	6-Mar-17	3328	INE204E01012
37	AGCNET	EQ	87	90.5	77.55	85.85	86	89.05	24600	2087232.4	6-Mar-17	336	INE676A01019
38	AGRITECH	EQ	29	32.25	29	30.3	30.2	30.8	19486	589749.8	6-Mar-17	38	INE449G01018
39	AGROPHOS	SM	21.45	22.5	21	22.25	22.1	21.5	162000	3590700	6-Mar-17	17	INE740V01019
40	AHLEAST	EQ	226.5	227	222	225	225	223	1688	379319.05	6-Mar-17	30	INE926K01017
41	AHLUCONT	EQ	313.05	323.65	306.05	310	308.5	318.35	8464	2636791.5	6-Mar-17	672	INE758C01029
42	AHLWEST	EQ	217.85	217.85	209.1	214.9	217.6	211.4	506	108682	6-Mar-17	10	INE915K01010
43	AIAENG	EQ	1445	1464.9	1435.1	1459.6	1459.2	1443.9	57974	84404907.05	6-Mar-17	2566	INE212H01026
44	AICHAMP	BE	26.4	27.5	26.4	27.5	27.5	26.25	26	687.5	6-Mar-17	2	INE768E01024
45	AIFL	EQ	387.95	400	381	385.25	388.45	380.55	52483	20342251.55	6-Mar-17	1594	INE428O01016
46	AJANTPHARM	EQ	1724.95	1734.3	1708.2	1717.5	1718.9	1723.4	51958	89390205.75	6-Mar-17	3929	INE031B01049
47	AJMERA	EQ	190.7	191.8	186.1	189.5	190	189.7	150233	28452803.6	6-Mar-17	4521	INE298G01027

System Design: 1.
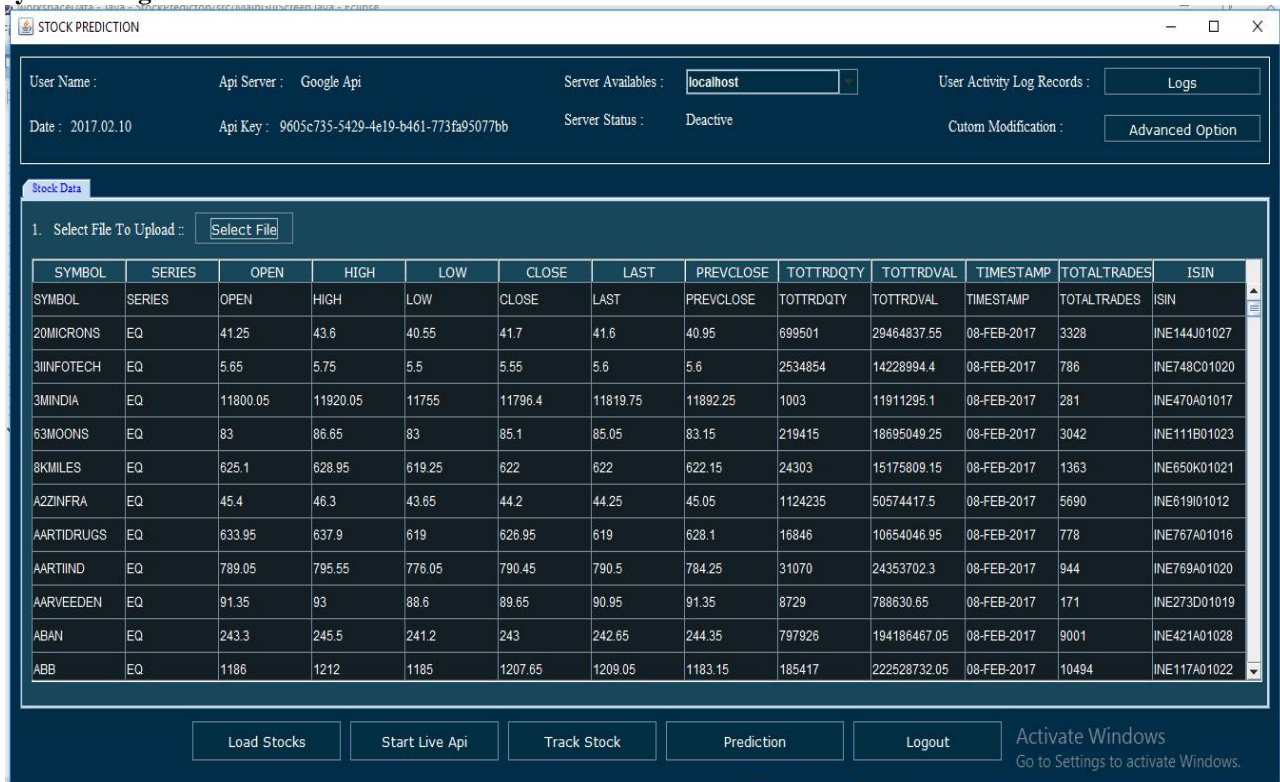
Fig1: Stock Prediction Module
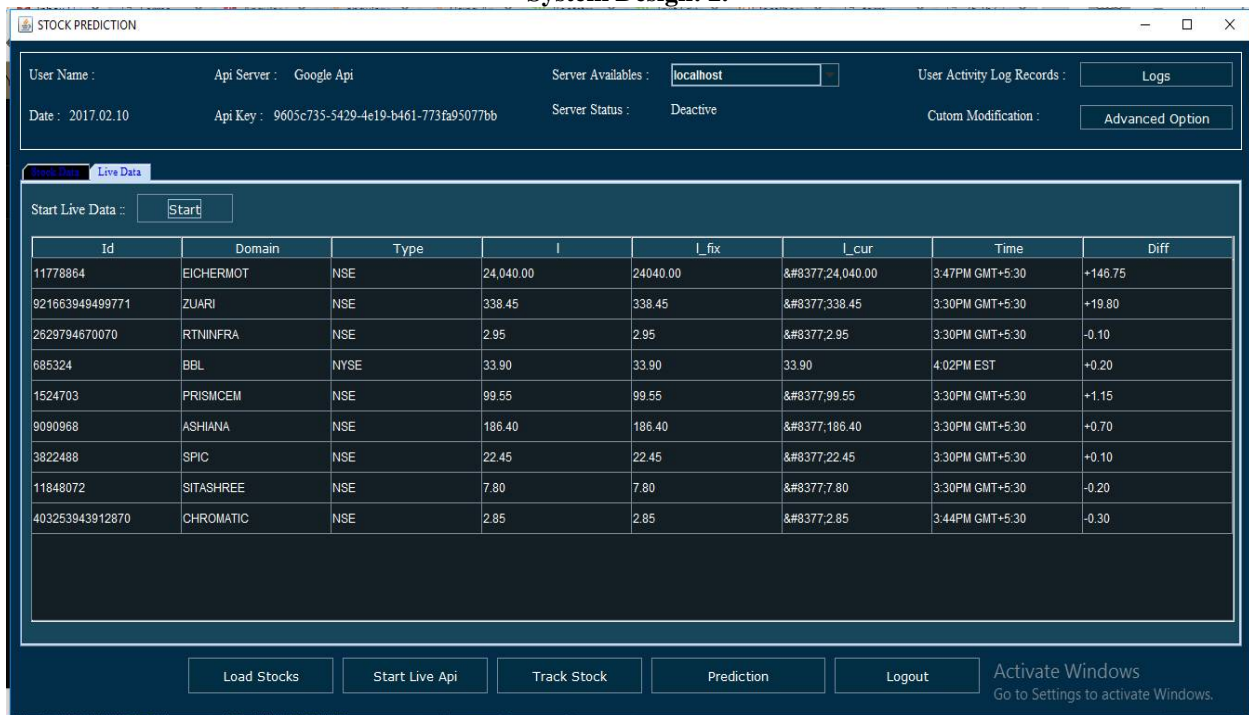
System Design: 2.

Fig2: Stock Prediction Module

System Design:3
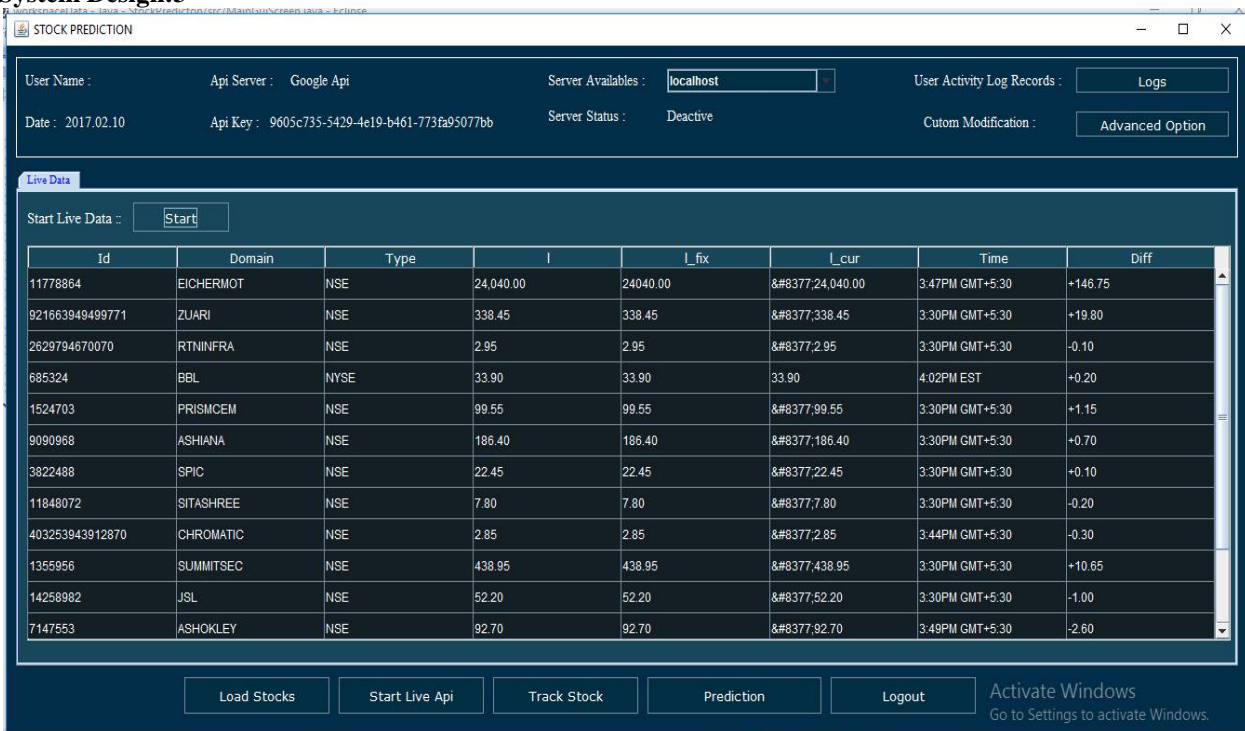
Fig3: Stock Prediction Module

VI. RESULT ANALYSIS

In our analysis we employed three different metrics namely, precison, recall & F1, which have been widely used in classifier performance analysis.

- **Precision:**

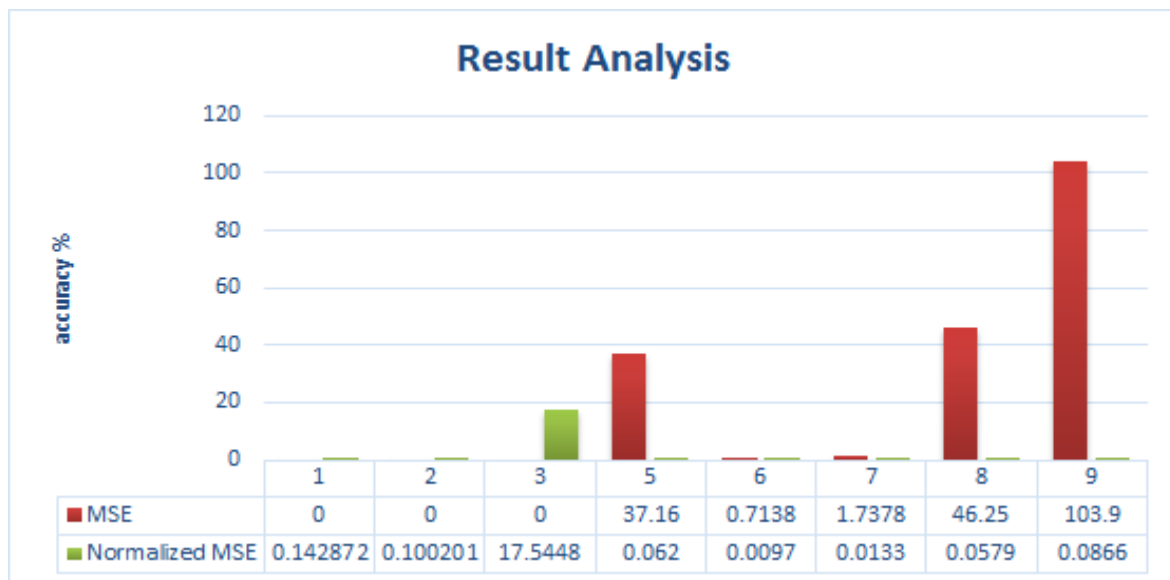Precision is the number of True Positives divided by the number of True Positives and False Positives i.e the number of positive predictions divided by the total number of positive class values predicted. It is also called the Positive Predictive Value (PPV).

- **Recall:**

Recall is the number of True Positives divided by the number of True Positives and the number of False Negatives i.e.it is the number of positive predictions divided by the number of positive class values in the test data. It is also called Sensitivity or the True Positive Rate.

- **F1 Score:**

The F1 Score is the 2*((precision*recall)/(precision+recall)). It is also called the F Score or the F Measure. Put another way, the F1 score conveys the balance between the precision and the recall.

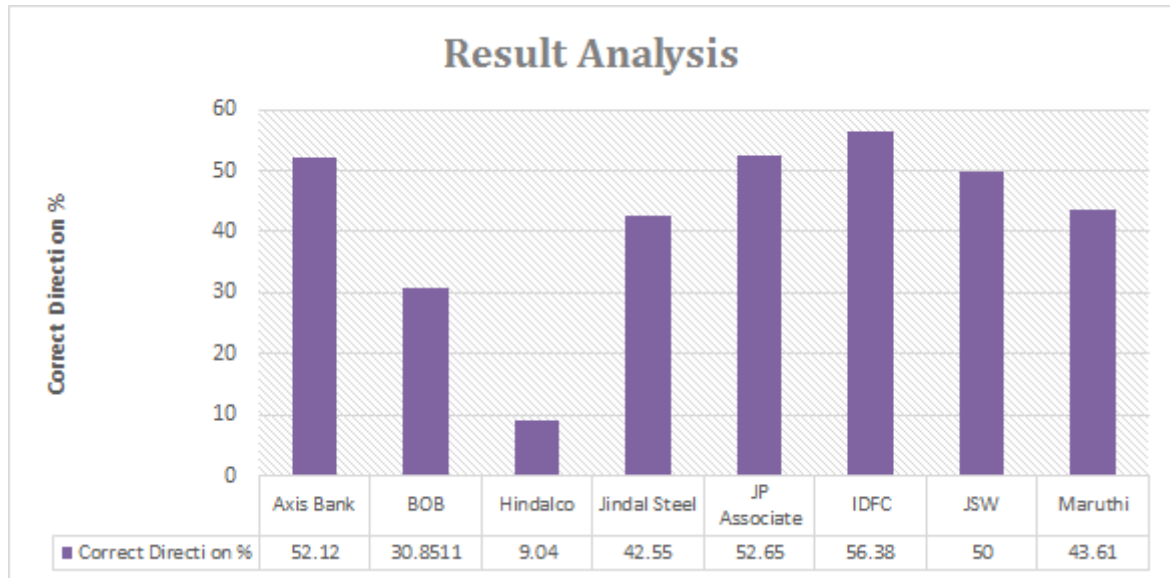|	1	2	3	5	6	7	8	9
■ MSE	0	0	0	37.16	0.7138	1.7378	46.25	103.9
■ Normalized MSE	0.142872	0.100201	17.5448	0.062	0.0097	0.0133	0.0579	0.0866

Result Analysis	Axis Bank	BOB	Hindalco	Jindal Steel	JP Associate	IDFC	JSW	Maruthi
Correct Directi on %	52.12	30.8511	9.04	42.55	52.65	56.38	50	43.61

VI. CONCLUSIONS

This research work will help the customer for decision making in share market. Furthermore, based on fuzzy rule based system stock exchange data could be used to overcome uncertainty, vagueness and imprecision of share market. This research aims to answer the research challenges by developing an optimal ensemble method for information discovery on the basis of DT Algorithm. This result shows that acceptable performance is obtained in a rapid change market.

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SYNTHESIS AND CHARACTERIZATION OF NOVEL QUINOLINONE CONTAINING THIABENDAZOLE

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ABSTRACT

The research and development of benzimidazole-containing drugs is an increasingly active and attractive topic of medicinal chemistry due to its ligand base approaches. The present work represents benzimidazole quinolinone based drugs along with new perspectives. It was synthesized by reacting 5-Amino-2-thiazol-4-yl-*1H*-benzimidazol and 7-hydroxy-4-methyl coumarin in presence of pyridine as a base and studied their antimicrobial activities.

KEYWORDS: Benzimidazole, Thiabendazole, Coumarin, Quinolinone and Antimicrobial Activity.

INTRODUCTION

Quinolines moiety are very interested due to their broad spectrum as anti-malarial[1-4], anticancer[5,6], antimicrobial[7], antibacterial[8,9], antifungal[10,11] and use as an inhibiting agent.[12] Quinoline based bacterial marketed drugs and malarial marketed drugs.[13] Many methods have developed for the synthesis of quinoline moiety.

Thiabendazole is a structurally analogous to benzimidazoles, well known as anthelminitic[5,14] and systemic fungicide. Its mode of action is systemic fungicide with protective and curative action.[9,15] Benzimidazole and thiazole analogous have found applications in medicine and agriculture.[10,16] Due to their electron-rich environment, Benzimidazole containing drugs bind to a variety of therapeutic targets, thereby exhibiting a broad spectrum of bioactivities.[17] Therefore an enormous medicinal value, the research and development of benzimidazole-containing drugs is an increasingly active and attractive topic of medicinal chemistry.

Experimental: All chemical reagents and solvents were synthetic grade commercial products [s.d. fine chemicals Ltd.] and distilled before use. Melting points were determined using open capillary method in the paraffin liquid and are uncorrected. I. R. spectra (cm^{-1}) were recorded on a Perkin Elmer RX1 FTIR spectrophotometer. The FAB mass spectra were recorded on a Jeol SX 102/Da-600 mass spectrometer and Elemental analyses were performed on a Perkin Elmer Series II CHNS Analyzer 2400. The purity and completion of compounds was checked by TLC.

I. Synthesis of 5-Amino-2-thiazol-4-yl-1*H*-benzimidazole (3): 5-Amino-2-thiazol-4-yl-1*H*-benzimidazole was synthesized and identified by comparing their spectrum data with reported values in the literature[18] or their melting points.
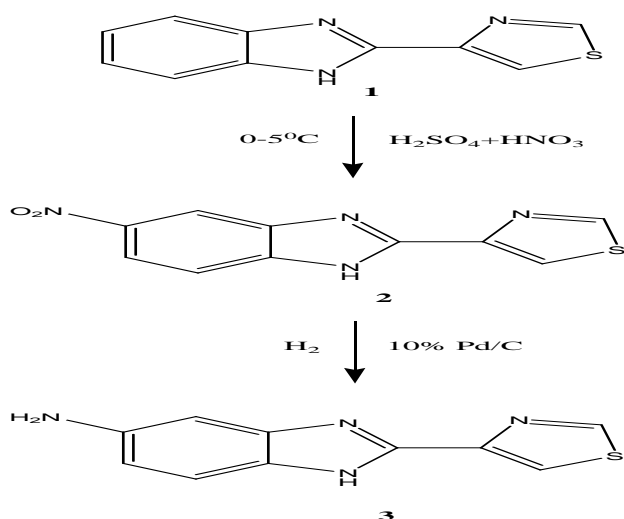
Procedure for 5-Nitro-2-thiazol-4-yl-1(3)*H*-benzimidazole (2): To a solution of a thiabendazole (1) in concentrated H$_2$SO$_4$ was added concentrated HNO$_3$ drop wise between 0 and 10°C. The mixture was stirred at room temperature for 2 h and then poured into ice water. Cautious neutralization with 50% NaOH provided a solid, which was filtered off and crystallized from MeOH to yield the desired product.

Light yellow solid, yield 55%, mp 242 °C, recrystallized from EtOH.

Procedure for 5-Amino-2-thiazol-4-yl-*1H*-benzimidazole (3)

One gram of a nitro derivative was dissolved in 100 mL of absolute ethanol, and the solution was reduced catalytically over 0.5 g of 10% palladium-on-charcoal at normal pressure and room temperature. After the uptake of hydrogen was complete, the catalyst was removed by filtration, and the solvent was evaporated in vacuo. Upon recrystallization, the pure compounds were obtained.

Light yellow solid, yield 62%, mp 233-235 °C, recrystallized from aqueous ethanol.
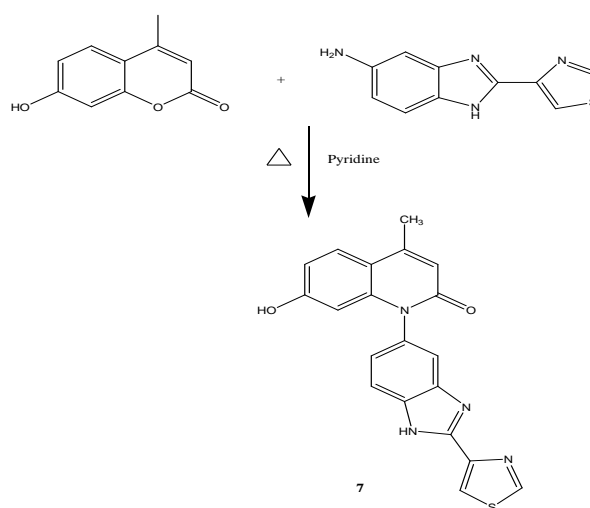
III. Synthesis of 7-hydroxy-4-methyl-1-(2-(thiazol-4-yl)-*1H*-benzo[*d*]imidazol-5-yl)quinolin-2(*1H*)-one: Solution of 7-hydroxy-4-methyl coumarin (3.52 gm 0.02 mole) and 5-aminothiabendazole (4.640 gm 0.02 mole) in pyridine was refluxed for 16 hours. After completion of reaction (TLC observed) the mixture was evapourated on roto evapourator. To this residue 100 ml water was added and make the pH 6 to 7 using dilute HCl solution. The precipitate obtained was filtered and washed with water and dried at 50 to 60^{0}C. To this crude product 100 ml ethanol was added and heated to get clear solution. Add 0.5 gm charcoal and filter the reaction mixture at hot condition. To this filtrate 100 ml water was added and stirred at room temperature for two hours. Filter the purified product and dried at 50 to 60^{0}C for 8 hours. Yield was found to be 86% and observed melting point was 186 to 188 ^{0}C.

II. Synthesis of 7-hydroxy-4-methyl coumarin[19]

150 ml conc. H_2SO_4 was stirred and cooled in an ice bath till the temperature was about 5 to 8^{0}C. 37 gm of finely powered resorcinol was dissolved in 50 ml ethyl acetoacetate until a clear solution was obtained. This resorcinol solution was slowly added into ice cold solution of H_2SO_4. The temperature of reaction mixture was maintained below 10^{0}C. The stirring was continued for half an hour. The reaction mixture was poured into ice water till solid product was separated. The crude product was recrystallized in ethanol. Yield was near about 80%. The melting point of purified product was 190-192 ^{0}C. Molecular formula is $C_{10}H_8O_3$.

7-hydroxy-4-methyl-1-(2-(thiazol-4-yl)-1*H*-benzo[*d*]imidazol-5-yl)quinolin-2(1*H*)-one

Table. 1: Characterization of synthesized compounds.

Compounds	M. F.	M. Wt.	M. P.	Yield	Elemental Analysis Cal(Found)
Thiabendazole[1]	$C_{10}H_7N_3S$	201.26	297 to 298 ^{0}C	------	C, 59.68(59.64); H,3.51(3.48); N,20.88(20.81);S,15.93(15.89)
5-Nitrothiabendazole[2]	$C_{10}H_6N_4O_2S$	246.25	240 to 243 ^{0}C	59%	C,48.78(48.78); H,2.46(2.41); N,22.75(22.65);O,12.99(12.91); S, 13.02(12.99)
5-Aminothiabendazole[3]	$C_{10}H_8N_4S$	216.26	233 to 235 ^{0}C	62%	C,55.54(55.48);H,3.73(3.65); N,25.91(25.86);S,14.83(14.79)
7-hydroxy-4-methyl coumarin[6]	$C_{10}H_8O_3$	176.05	190 to 192 ^{0}C	80%	C,68.18(68.11); H,4.58(4.67); O,27.25(27.18)
Quinolino-thiabendazole[7]	$C_{20}H_{14}N_4O_2S$	374.42	186 To 188 ^{0}C	86%	C, 64.16(64.12); H, 3.77(3.70); N, 14.96(14.89); O, 8.55(8.49); S, 8.56(8.47)

Table. 2: I R data of synthesized compounds.

Band	TBZ [1] cm⁻¹	5-NH₂-TBZ[3] cm⁻¹	[7]cm⁻¹
N-H stretch	3093	3387, 3302, 3116	3244, 3093
N-H vibration	1095	---	----
υ (C=N)imidazole	1589	1496	1546
υ (C=N)thiazole	1419	1411	1481
C-S stretch	1296	1357	1280
-C=O stretch	---	---	1639
-OH stretch	---	---	3344

Mass of Compound 7 (m/z): 373.08, 248.85, 214.96, 154.94

RESULTS AND DISCUSSION

In this study, the structure of the synthesized compounds was elucidated by means of IR, Elemental analysis and Mass. All the compounds were evaluated for antibacterial and antifungal activities by Disc diffusion method.[20-21] The antimicrobial activity of tested compounds against different strains of bacteria and fungus is shown in (Table 3). The newly synthesized compound was evaluated for their in-vitro antibacterial activity against gram positive bacteria i) *Staphylococcus aureus ii) Staphylococcus aureus* (MRSA), iii) *Bacillus subtilis* and gram negative bacteria i) *Pseudomonas aeruginosa ii) Escherichia coli* and antifungal activity against i) *Aspergillus niger ii) Candida albicans*. The zone of growth inhibition values was determined by comparison to standard drugs (Chloramphenicol, Methicillin and Amphotericin B).

Table 3: Antimicrobial data of synthesized compounds

Sr. No.	Sample code	*S. aureus*	*S. aureus* (MRSA)	*B. subtilis*	*E. coli*	*P. aeruginosa*	*C. albicans*	*A. niger*
1	Compound **7**	13.70	NA	18.11	14.84	10.08	-	-
2	Chloramphenicol	24.47	NA	20.05	26.68	14.18	NA	NA
3	Methicillin	NA	8.74	NA	NA	NA	NA	NA
4	Amphotericin B	NA	NA	NA	NA	NA	20.15	10.27

In general, the results of antibacterial evaluation of the test compound in comparison with the reference drugs indicated that compound showed comparable potent antibacterial activity with respect to the reference drugs against all tested species. But for Methicillin Resistance *Staphylococcus aureus* (MRSA) reveal that target compound dose not shown activity. The same case of antifungal data does not shown antifungal potency as compared to Amphotericin B.

ACKNOWLEDGEMENT

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Studies of Stability constant of dompridone with transion metal ions in mixed solvent at 303K.

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Abstract:-

The interaction of transition metal ion with domperidone drug have been investigated by pH metric titration at 0.1 M ionic strength at room temperature in 50 % dioxane-Water mixture. The data obtained use to estimate the values of proton-ligand stability constant (P^k) and Metal -ligand stability constant (logK). It is observed that transition metal ions form 1:1, 1:2 complexes with all the systems.

Key word: - Stability constant, transition metal.

Introduction: -

It is used as an antiemetic, gastroprokinetic agent, and galactagogue. The studies of metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport f metal ion in the biological kingdom.

In the earlier papers extensive data base on metal complexes with substituted heterocyclic drugs was presented.

Narwade et.al. [1] studies the Formation and Stability constant of thorium (IV) complex with some substituted pyrazolines. Mathieu W.A. Steenland et.al.[2] studies stability constant of Cu(II) and Ni(II) complexes of trans –dioxopentaaza macrocycles in aqueous solution by different technique. Hong-Wen Gaoet.al.[3] has studied the stability constant of Cu (II) and Co (II) complexes with CNBAC in water sample spectrophotometrically. Tuba Sismanoglu [4] have studied the stability constant of binary complexes of Nicotinamide with Mn (II) by pH metrically. He also determines change in free energy, change in enthalpy and change in entropy from stability constant at different temperature. Tekade et.al. [5] have been studied complex formation of Cu (II) and Co (II) metal ion complex with substituted isoxazolines. O.Yamauchi et.al. [6] studied stability constant of metal complexes amino acids with charged side chain by pH–metrically. Hayati Sari et.al.[7] studied the stability constant of glyoxime derivative and their Nickel, Copper, Cobalt and Zinc complexes potentiometric and theoretically.

After review of literature survey the detail study of complex under identical set of experimental condition is still lacking. It was thought of interest to study the chelating properties of substituted heterocyclic drug under suitable condition with lanthanide by pH metrically.

Material and Method:-

pH measurement were carried out with equip-tronic EQ-610 pH meter (aceuracy ± 0.01 units) using combine glass electrode at room temperature. Metal nitrate prepared in triply distill water and concentration estimated by standard method.[8] The solution of drugs prepared in solvent .The pH metric reading in 50% 1,4 dioxane - water mixture were converted to $[H^+]$ value by applying the correction proposed by Van Uitert Haas.

The overall ionic strength of solution was constant and calculated by the equation
$$\ldots \tilde{1} \ldots C_i\, Z_i^2$$

The concentration of other ion in addition to Na^+ and ClO^-_4 were also taken into consideration.

Result and discussion:-

Substituted heterocyclic drugs may be ionized as acid having replaceable H^+ ion from -OH group. Therefore it is represented as HL i.e.

$$HL \longrightarrow H^+ +L^-$$

The titration data used to construct the curves between volume of NaOH and P^H. They are called acid-ligand titration curves.

It is observed from titration curves for all systems ligand start deviating from the free acid curves at P^H = 2.5 and deviating continuously up to P^H =12. The deviation shows that dissociation of proton in substituted drugs.

The average number of proton associated with the ligand (n_A) was determined from free acid and acid – ligand titration curves employing the equation of Irving and Rossotti [9] . The P^k values were determined from formation curves (n_A $_v^s$ P^H) by noting the P^H at which n_A =0.5. The accurate values of pk were calculated by point wise calculations which are presented in table -1.

Table-1 - DETERMINATION OF PROTON-LIGAND STABILITY CONSTANT (pK) OF DRUG AT 0.1M IONIC STRERNGTH.

System	Constant pK	
	Half integral	Point wise calculation
Ligand	7.45	7.275. ± 0.05

METAL -LIGAND STABILITY CONSTANT (Log k):-

Metal-ligand stability constant of transition metal chelate with substituted heterocyclic drug were determined by employing Bjerrum calvin P^H metric titration method as adopted by Irving and Rossotti. The formation of chelate between metal ions with some substituted heterocyclic drug was indicated by the significant separation starting from pH =2.5 for all system.

Table-2 - DETERMINATION OF METAL - LIGAND STABILITY CONSTANT (logK) OF TRANSITION METAL IONS WITH DRUG AT 0.1M IONIC STRERNGTH.

System	Metal ion	$Logk_1$	$Logk_2$	$Logk_1 - Logk_2$	$Logk_1 / Logk_2$
Ligand 1	Cu(II)	3.65	6.45	2.80	1.7671
	Zn(II)	4.95	6.50	1.55	1.3131
	Ni(II)	4.85	6.60	1.75	1.3608
	Mg(II)	4.55	5.75	1.20	1.2637
	Fe(II)	5.30	6.75	1.45	1.2736

The result shows the ratio of $Logk_1 / Logk_2$ is positive in all cases. This implies that there is little or no steric hindrance to the addition of secondary ligand molecule .The smaller difference may be due to trans structure.

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Viscometric Studies of Substituted Heterocyclic Drug Rosuvastatin at Various Molar Concentrations At 303 K.

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Abstract :

In present study, the viscometric study of substituted heterocyclic drugs Rosuvastatin were measured at different concentration by keeping temperature constant at 303 K in different solvent ethanol and methanol. The obtained data has been used to calculate relative viscosity and viscosity coefficient (A, β) by using john–dole equation. These parameters throw the light on the solute-solvent interaction and solute-solute interaction.

Key word: Rosuvastatin, ethanol, methanol, viscosity coefficient.

Introduction

Viscosity is one of the physical properties of liquid which implies resistance to flow due to the internal friction of liquid molecules. The measurement of viscosity provides useful information about solute-solute and solute –solvent interaction in non aqueous and aqueous solvents[1-3]. The density, refractive index, viscosity and surface tension of liquid mixture give very useful analytical information for industrial purpose[4-5]. The viscosity measurement of solution plays a vital role in pharmaceutical, industrial, medicinal, agricultural, biochemical and drug sciences[6-10]. It provides brief information regarding molecular weight of the solute, solute-solute, solute-solvent and solvent-solvent interactions. Hence, Viscosity measurement is very essential to know the constituents and arrangement of any molecule. The number of activities in vivo of the drug like absorption, transmission and its effect will directly relate to viscosity measurements and solvent interactions in the human anatomy and life sciences[11-13]. Study of the viscosity measurements is user-friendly, sensitive and precise. Tayade et al[14] have been investigated the viscometric study of 5-p-Tolylthiocarbamido 1-naphthol at different molar concentrations and at 298 K in 70% ethanol-water mixture. They are observed that the density and relative viscosity of drugs decreases with decreasing concentration of solution. The viscometric studies of N-(3-substituted) phenyl-4-methoxy phenyl schiff bases in water-dioxane mixture at various percentage compositions in dioxane-water medium has been investigated by Khan[15]. Wadekar et al[16] have been investigated The viscometric study of substituted 2-oxo-2-h-chromene-3-carbohydrazide derivatives in 70% DMF- Water at different temperature. Kshirsagar and Tayade[17] have been investigated the study of S-substituted triazinothiocarbamides in dioxane water mixture at 303 K in 60% dioxane-water mixture at different concentration 0.1 M, 0.075 M, 0.56 M and 0.042 M. It is observed that the negative values of A and β-coefficient characterized as 'structure-breaker' indicating a weak solute-solvent interaction which is good for interactions in between the drug and the drug receptors shows best drug activity and drug effect and it favors pharmacokinetics and pharmacodynamics of drug. The studies on viscosity, density and refractive index of

substituted heterocyclic compound in 30 % dioxane-water solvent at 303 K and at different concentration have been reported by Sonar[18]. Therefore in the present work the systematic study of substituted heterocyclic drugs Rosuvastatin viscometrically in the concentration range 0.01, 0.005, 0.0025, 0.00125 and 0.000625 M in different solvent ethanol and methanol at 303K.

Materials and Method:

All the chemicals used are of good analytical grade (AR). The solvent ethanol was purified by the method described by Vogel[19]. The solution of the ligand was prepared by dissolving required amount of ligand in purified ethanol and methanol solvent. The density of solvent and solutions were measured by specific gravity bottle having 10 ml capacity. For viscosity measurement Ostwald's viscometer was used. The flow time was measured by using digital clock (0.01 Sec). The constant temperature was maintained by circulating water through the double wall measuring cell, made up of glass.

Observations and Calculation

The relative viscosity of each solution is determined by following empirical formula,

$$\eta_r = (d_s \times t_s) / (d_o \times t_o) \qquad \ldots\ldots\ldots (1)$$

Where, η_r is relative viscosity of ligand solution, d_s is density of ligand solution,

d_o is density of solvent, t_o is time of flow for solvent,

t_s is time of flow for ligand solution.

The relative viscosities have been analyzed by Jones-Dole equation

$$(\eta_r - 1) / \sqrt{C} = A + \beta\sqrt{C} \qquad \ldots\ldots\ldots (2)$$

Where, C is the molar concentration of the ligand solution. A is the Falkenhagen coefficient which is the measure of solute-solute interactions and β is the Jones-Dole coefficient which is the measure of solute-solvent interactions.

The graphs are plotted between $(\eta_r - 1)/\sqrt{C}$ against $\sqrt{C}$. The graph for each system gives linear straight line showing validity of Jones-Dole equation. The slope of straight line gives value of β-coefficient and intercept gives the value of Falkenhagen coefficient A. The plots of $(\eta_r - 1)/\sqrt{C}$ against $\sqrt{C}$ for all the ligand systems are shown in Fig 1 and 2.

Table: 1 The values of η_r, Density, $\eta_{sp}/\sqrt{C}$ of substituted heterocyclic drug in Ethanol.

Conc. Mol./lit	Density Kg/m^3	Flow time (Sec)	η_r	$\eta_{sp}/\sqrt{C}$	A	β
		Rosuvastatin + Ethanol				
1×10^{-2}	8203.0	267	1.362	3.6294		
5×10^{-3}	8179.0	250	1.272	3.8533		
2.5×10^{-3}	8160.0	240	1.218	4.3739	5.114	-15.66
1.25×10^{-3}	8147.0	229	1.160	4.5533		
0.625×10^{-3}	8137.0	221	1.119	4.7620		

Table:2 The values of η_r, Density, $\eta_{sp}/\sqrt{C}$ of substituted heterocyclic drug in Methanol.

Conc. Mol./lit	Density Kg/m^3	Flow time (Sec)	η_r	$\eta_{sp}/\sqrt{C}$	A	β
			Rosuvastatin + Methanol			
1×10^{-2}	8060.0	166	1.433	4.3339		
5×10^{-3}	8037.0	156	1.343	4.8535		
2.5×10^{-3}	8020.0	148	1.271	5.4323	8.043	-40.99
1.25×10^{-3}	8009.0	143	1.226	6.4197		
0.625×10^{-3}	8001.0	139	1.191	7.6584		

Results and Discussion

In the present work, the density and relative viscosity of solution increases with increase in the concentration of solution for both the solvents. The increase in viscosity with increase in concentration is due to the increase in the solute-solvent interactions. This may be due to the fact that when the concentration increases, the number of solute molecules increases and at that time percentage of solvent molecules decreases in the solution which is responsible to decrease solvation effect. i. e. increases the solute-solvent interactions. The values of coefficient A and coefficient β are shown in table- 1 and 2. The small and larger value of Falkenhagen coefficient A shows the weaker and stronger solute-solute interaction respectively. The values of Falkenhagen coefficient (A) are positive for both the ligands indicates that there is strong solute-solute interaction in the solute molecules. The values of Jones-Dole coefficient β may be positive or negative. It is observed that the values of Jones-Dole coefficient β are negative for both the solvents. It is a measure of disorder introduced by the solute into the solvent. The negative values of Jones-Dole coefficient β are characterized as "structure breaker" which indicating weak interaction between solute and solvent molecules. The weak solute-solvent interaction may be due to the strong hydrogen bonding is present in solution and in a dilute solution the solute molecules can disrupt this hydrogen bonding to lesser extent.

Fig. 1 Plots of $\eta_{sp}/\sqrt{C}$ Vs $\sqrt{C}$ (Rosuvastatin + Ethyl alcohol)

Fig. 2 Plots of $\eta_{sp}/\sqrt{C}$ Vs $\sqrt{C}$ (Rosuvastatin + Methyl alcohol)
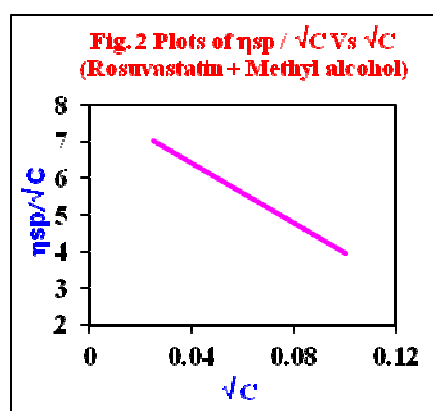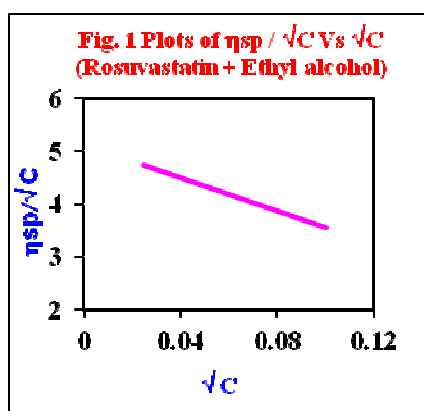
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STUDY OF ACOUSTICAL PROPERTIES OF SCHIFF BASE OF (5-HYDROXY - 3 -METHYL - 1 - (2, 4- DINITROPHENYL) – PYRAZOL – 4 - YL) (PHENYL) METHANONE AND 2-AMINO 5-BROMO PYRIDINE IN MIX SOLVENT AT 303 K .

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Abstract

The investigation of ultrasonic velocity, density from acoustical properties of Schiff base of (5-hydroxy -3-methyl-1-(2,4dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and acoustical properties in mix solvent system and constant temp 300 K. from these measurement data obtained are used to calculate some acoustical parameter such as adiabatic compressibility (s), Partial molal volume (v), intermolecular free length (Lf), apparent molal compressibility (k), specific acoustic impedance (Z), relative association (RA) and solvation number (Sn).

Key word: - Schiff base, pyrazolone, *Ultrasonic velocity, viscosity, apparent molal volume.*

Introduction :

Ultrasonic velocity is one important property of compound to Study the interpreted solute-solvent, ion-solvent interaction in aqueous and non aqueous medium[1-4]. Meshram et. al. investigate for some substituted Pyrazolines different acoustical properties in binary mixture acetone-water and observed variation of ultrasonic velocity with concentration[5]. Palani have examined the measurement of ultrasonic velocity and density of amino acid in aqueous magnesium acetate at constant temp[6]. By considering size of ion and polarity of solvent ion-ion interaction can be determine and the strength of this interaction is directly proportional to the size of the ions and magnitude of dipole but inversely proportional to the distance between ion and molecules. Voleisines et al. has been studied the structural properties of solution of lanthanide salt by measuring ultrasonic velocity[7]. Tadkalkar et.al. have studied the acoustical properties and thermodynamic properties of citric acid in water at different temperature[8].

After review of literature we observed that there is no study under identical set of experimental condition for Schiff base of Pyrazolone with 2-amino 5-bromo pyridine. It attract our interest toward the Schiff base of (5-hydroxy -3-methyl-1-(2,4dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and 2-amino 5-bromo pyridine acoustical properties study under suitable condition.

Experimental

The Novel synthesized Schiff base of (5-hydroxy -3-methyl-1-(2,4dinitrophenyl)-pyrazol-4-yl)(phenyl)methanone and 2-amino 5-bromo pyridine was used for present study. The ligands of the Schiff base were synthesized according to literature process. The double distilled Dioxane is used for preparation of different concentration of Schiff Base solution and it will be purified by Vogel's standard method[9]. The densities were determined by using

specific gravity bottle by relative measurement method with accuracy 1×10^{-5} gm/cm^3. The ultrasonic velocities were measured by using ultrasonic interferometer having frequency 3MHz .The constant temperature was maintained by circulating water through the double wall measuring cell, made up of steel.

In the present analysis, different acoustic properties such as intermolecular free length (Lf), adiabatic compressibility (bs), apparent molal volume (fv), apparent molal compressibility (fk),relative association (RA), specific acoustic impedance (Z), limiting apparent molal compressibility (f^{0}k), limiting apparent molal volume(f^{0}v), solvation number(Sn) and their constant (Sk, Sv) have been evaluated

Results and Discussion :

In the present study, different acoustical properties are recorded it shown in table-1, table-2 and table-3 It was found that when concentration for system increase Intermolecular free length(Lf) decrease linearly and hence increased in ultrasonic velocity are observed. It was occurred due to strong interaction between solvent and ion molecules suggesting a structure promoting behavior of the added electrolyte. The specific acoustic impedance (Z) increased with the increase in concentration of Schiff base of benzoyl Pyrazolone in 10% dioxane. As the concentration of solution increases, the adiabatic compressibility is decreases. The decrease in to collection of solvent molecule around solute molecules indicates that there are solute-solvent interaction are presence. This indicates that there is strong interaction between solvent and solute molecule in solution and the solution is becoming more and more compressible. It was observed that concentration in system is increases the apparent molal volume also increases. It indicates the existence of strong interaction between solvent and solute molecule. It was initiated that the value of apparent molal compressibility was decreased with the increase in concentration of Schiff base, it shows weak electrostatic attraction force between the close vicinity of ions. So there are weak molecular association was found in Schiff base Pyrazolone.

The value of relative association decreased as the concentration in system increases. There was a decrease in solvation number as the concentration in system increases; it indicates the strong coordination bond forms by solvent molecule in primary layer. And due to this decrease in size of secondary layer of Solvation are observed. The value of Sk exhibits negative. It indicates the weak solute-solute or ion-ion interactions in Schiff base of benzoyl Pyrazolone system are present. From table-3, It was observed that the value of limiting apparent molal volume is positive. It indicates that the ion-dipolar interaction in Schiff base of benzoyl Pyrazolone and 1, 4 dioxane. The all value of Sv are positive, indicates the strong interaction between solvent and solute molecule. These value indicates an induced effect of 1, 4 dioxane on solvent- solute interaction. From fig. 1 and 2 the value of Sk and Sv has been determine. It was also observed that the value of apparent molal compressibility was decreased with the increase in concentration of Schiff base. It shows weak electrostatic attraction force between the close vicinity of ions. The value of relative association decreased as the concentration in system increases. It has been observed that there was weak interaction between solvent- solute. There was a decrease in solvation number as the concentration in system increases; it indicates the strong coordination bond forms by solvent molecule in primary layer.

Table-1 Ultrasonic velocity, density, adiabatic compressibility (β_S), Specific acoustic impedance (Z) Intermolecular free length (L_f).

Concentration moles lit^{-1} (m)	Density (ds) kg m^{-3}	Ultrasonic velocity (Us) m s^{-1}	Adiabatic compressibiliy (β_S) x10^{-10} m^{2}N^{-1}	Intermolecular free length (L_f) x10^{-11} m	Specific acoustic impedance (Zx10^6) kg m^{-2} s^{-1}
Schiff base of benzoyl pyrazolone + 10% 1,4 Dioxane					
1x10^{-3}	1019.93	1490	4.43252	4.2343	1.5168
2x10^{-3}	1020.09	1495	4.41747	4.2271	1.5195
3x10^{-3}	1020.23	1507	4.38845	4.2132	1.5246
4x10^{-3}	1020.36	1515	4.31823	4.1794	1.5371
5x10^{-3}	1020.48	1519	4.26994	4.1559	1.5458
6x10^{-3}	1020.59	1529	4.24922	4.1458	1.5497
7x10^{-3}	1020.68	1537	4.18896	4.1163	1.5609
8x10^{-3}	1020.76	1541	4.14943	4.0969	1.5684
9x10^{-3}	1020.83	1545	4.12331	4.0839	1.5734

Table-2 Concentration (m), Relative association (R_A), Apparent molal compressibility ( ), Apparent molal volume (ϕ_v) , Solvation number (S_n)-

Concentration (m) moles lit^{-1}	Apparent molal volume (ϕ_v) m^{3}mole^{-1}	Apparent molar compressibility (ϕ_k x10^{-10} m^{2}N^{-1})	Relative association (R_A)	Solvation number (S_n)
1x10^{-3}	0.34001	2.26646	0.99937	0.99641
2x10^{-3}	0.34957	2.25117	0.99792	0.98969
3x10^{-3}	0.359134	2.21471	0.99408	0.97366
4x10^{-3}	0.366296	2.18956	0.99144	0.96260
5x10^{-3}	0.372499	2.17864	0.99038	0.95780
6x10^{-3}	0.378224	2.14740	0.98699	0.94407
7x10^{-3}	0.385053	2.12687	0.98476	0.93504
8x10^{-3}	0.39137	2.11326	0.98330	0.92906
9x10^{-3}	0.397347	2.10309	0.98222	0.92459

Table-3 Limiting Apparent molal compressibility ($\tilde{}$), Limiting Apparent molal volume ($\tilde{}_v$), S_v and S_k

Ligand	Limiting Apparent molal volume (^0_v) m^{3}mole^{-1}	Limiting Apparent molal compressibility ( )x10^{-10} m^2 N^{-1}	S_v m^{3}kg$^{1/2}$mole$^{-3/2}$	S_k m^{3}mole^{-2}kg.N^{-1}
Schiff base of pyrazolone	0.3362	2.2839	6.9753	-21.41
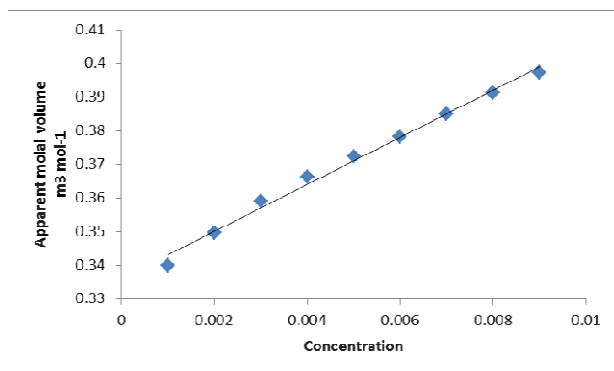
Fig.-1 -Apparent molal volume (m³mole⁻¹)
Vs Concentration (mole lit⁻¹)
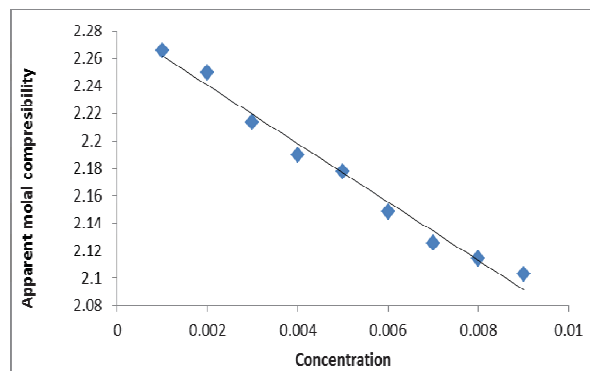

Fig.-2- Aparent molar compressibility10^{-9}
(m² N⁻¹)   Vs Concentration (mole lit⁻¹)

Conclusion

In present study the acoustical properties were calculated from experimental data ,it shows that there are interaction between solute-solute or ion-ion and solvent-solute exists between Schiff base of (5-hydroxy -3-methyl-1-(2,4dinitrophenyl)-pyrazol-4-yl)(phenyl) methanone and 2-amino 5-bromo pyridine in 10% 1,4 dioxane . And from the experimental data it is concluded that the interaction between solute and solvent in Schiff base of benzoyl Pyrazolone & dioxane systems are strong.

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STUDIES OF STABILITY CONSTANT OF N'-((5-CHLORO-3-METHYL-1-PHENYL-PYRAZOL-4-YL) METHYLENE) ISONICOTINOHYDRAZIDE WITH TRANSION METAL IONS AT 303K.

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ABSTRACT

The interaction of transion metal ion with of N'-((5-chloro-3-methyl-1-phenyl-Pyrazol-4-yl) methylene) isonicotinohydrazide drug have been investigated by pH metric titration at 0.08 M ionic strength at room temperature in 30% Ethanol-Water mixture. The data obtained use to estimate the values of proton-ligand stability constant (P^k) and Metal -ligand stability constant (logK). It is observed that transition metal ion form 1:1, 1: 2 complexes with all the systems.

KEYWORD: *The interaction isonicotinohydrazide stability constant (logK).*

INTRODUCTION

The studies of metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport f metal ion in the biological kingdom.

In the earlier papers extensive data base on metal complexes with substituted heterocyclic drugs was presented.

Narwade et.al.[1] studies the Formation and Stability constant of thorium (IV) complex with some substituted pyrazolines. Mathieu W.A. Steenland et.al.[2] studies stability constant of Cu(II) and Ni(II) complexes of trans –dioxopentaaza macrocycles in aqueous solution by different technique. Hong-Wen Gaoet.al.[3] has studied the stability constant of Cu (II) and Co (II) complexes with CNBAC in water sample spectrophotometrically. Tuba Sismanoglu [4] have studied the stability constant of binary complexes of Nicotinamide with Mn (II) by pH metrically. He also determines change in free energy, change in enthalpy and change in entropy from stability constant at different temperature. Tekade et.al.[5] have been studied complex formation of Cu (II) and Co (II) metal ion complex with substituted isoxazolines. O.Yamauchi et.al.[6] studied stability constant of metal complexes amino acids with charged side chain by pH–metrically. Hayati Sari et.al.[7] studied the stability constant of glyoxime derivative and their Nickel, Copper, Cobalt and Zinc complexes potentiometric and theoretically.

After review of literature survey the detail study of complex under identical set of experimental condition is still lacking. It was thought of interest to study the chelating properties of substituted heterocyclic drugs under suitable condition with lanthanide by pH metrically.

Experimental Details

The Schiff base ligands were synthesized according to literature process.[10-12] The structures were confirmed by NMR, IR and purity of these compounds was verified by TLC and melting points.

The stock solution of Schiff base was prepared in 30 % Ethanol-Water mixture by dissolving the requisite quantity of the ligands in a minimum volume of solvent subsequently diluted to the final volume. The ligands were acidified with $HClO_4$ in a 30 % Ethanol-Water mixture and the overall ionic strength of solution was constant maintains by adding (0.1M) $NaClO_4$ The solutions were titrated with standard NaOH (0.2N) solution.

The following three solutions were titrated separately against standard NaOH
1. Free $HClO_4$ (A).
2. Free $HClO_4$ + Ligand (A+L).
3. Free $HClO_4$ + Ligand +Metal ion (A+L+M).

The pH meter reading were taken after fixed interval until stable reading was obtained and data obtained from

each titration is plotted as pH Vs volume of NaOH added.

MATERIALS AND METHOD

pH measurement were carried out with equip-tronic EQ-610 pH meter (accuracy $\pm$ 0.01 units) using combine glass electrode at room temperature. Metal ions solution were prepared in triply distill water and concentration estimated by standard method.[8] The solution of drug prepared in solvent .The pH metric reading in 30% ethanol – water mixture were converted to $[H^+]$ value by applying the correction proposed by Van Uitert Haas.
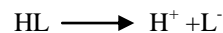
The overall ionic strength of solution was constant and calculated by the equation

$$\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box\Box C_i Z_i^2$$

The concentration of other ion in addition to Na^+ and ClO_4^- were also taken into consideration.

RESULT AND DISCUSSION

Substituted heterocyclic drugs may be ionized as acid having replaceable H^+ ion from -NH group. Therefore it is represented as HL i.e.

$$HL \longrightarrow H^+ + L^-$$

The titration data used to construct the curves between volume of NaOH and P^H. They are called acid-ligand titration curves.

It is observed from titration curves for all systems ligand start deviating from the free acid curves at P^H 5.0 and deviating continuously up to P^H =10. The deviation shows that dissociation of proton in substituted drugs.

The average number of proton associated with the ligand (n_A) was determined from free acid and acid – ligand titration curves employing the equation of Irving and Rossotti.[9] The P^k values were determined from formation curves (n_A $_v^s$ P^H) by noting the P^H at which n_A =0.5. The accurate values of pk were calculated by point wise calculations which are presented in table -1. The pK values are found.

Table-1: Determination of proton- ligand stability constant (pK) at 0.08M ionic strength

System	Constant pK	
	Half integral	Point wise calculation
Ligand-1	9.2	9.04. $\pm$ 0.05

METAL -LIGAND STABILITY CONSTANT (Log k)

Metal-ligand stability constant of transition metal ion chelate with drug were determined by employing Bjerrum calvin P^H metric titration method as adopted by Irving and Rossotti. The formation of chelate between transition metal ion with drug was indicated by the significant separation starting from pH =5.0 for transition metal ion with ligand -1.

Table-2: Determination of metal –ligand stability constant (logK) of transition metal ion with drug at 0.08M ionic strength.

stem	$Logk_1$	$Logk_2$	$Logk_2 - Logk_1$	$Logk_2 / Logk_1$
Fe(II)-Ligand	5.5	8.0	2.5	1.45
Co(II)-Ligand	5.3	7.3	2	1.38
Ni(II)-Ligand	5.0	6.85	1.85	1.37
Cu(II)-Ligand	5.4	7.15	1.75	1.32
Zn(II)-Ligand	5.4	7.2	1.8	1.33

The result shows the ratio of $Logk_2 / Logk_1$ is positive in all cases. This implies that there is little or no steric hindrance to the addition of secondary ligand molecule.

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